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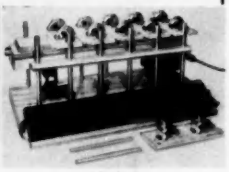

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OCTOBER 1960
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TEXTILE RESEARCH JOURNAL

Cotton Quality Study

V: Resistance to Abrasion

John P. McNally[1] and Frank A. McCord[2]

National Cotton Council of America, Memphis, Tennessee

Introduction

Cotton's satisfactory wearing qualities have long been held in high regard by consumers. A major reason for this is cotton's ability to resist damage from abrasion or rubbing. In recent years, however, competition from certain synthetic fibers, particularly nylon, has made reappraisal of cotton's abrasion performance desirable. Moreover, increasing use of chemical finishes to enhance such qualities as mildew, soil, and wrinkle resistance intensifies the need for good abrasion resistance in cotton textiles.

Abrasion resistance is a textile quality which is perhaps taken for granted by the consumer, especially in apparel uses. Unlike color or luster, it is not easily evaluated at the time of purchase. Nevertheless, resistance to abrasion is a consideration in a sizeable portion of cotton textile markets. Market studies indicate that consumers consider abrasion resistance to have some importance in end uses that consume more than two billion pounds of cotton textiles annually. Improvements in abrasion resistance would strengthen cotton against competitive losses in current markets consuming nearly 800 million pounds yearly and at the same time provide an opportunity for cotton to achieve gains against other materials equal to over 600 million pounds yearly. The incentive for undertaking research to improve the abrasion performance of cotton is strong, therefore.

This study discusses cotton's market potential through improved abrasion resistance, reviews technology related to abrasion resistance, and suggests research that might well contribute to increasing markets for cotton.

The Market Significance of Abrasion Resistance

From the consumer viewpoint, abrasion resistance is a factor in virtually every textile application. This is particularly true for cotton products which customarily are subjected to hard usage and to severe reconditioning processes. Improvements in abrasion resistance alone, however, will not necessarily strengthen cotton's competitive position in all uses nor expand consumption, because inherent qualities which contribute to good abrasion resistance already provide cotton with performance characteristics which are adequate for many purposes and which are superior to the abrasion resistance of most competing materials. Furthermore, other qualities assume far more importance in some outlets than abrasion resistance.

Continuing market studies and evaluations of consumer quality requirements in products accounting

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TABLE I. Relative Importance of Abrasion Resistance by End Uses *

	Gross wt. of fabric & yarn (1,000 lb. cotton equiv.)	Percent cotton	Cotton (1,000 lb.)	Other materials (1,000 lb. cotton equiv.)
PART A: Consumption of Materials in Uses in Which Abrasion Resistance is a Major Consideration				
Total	**2,205,387**	**37**	**822,347**	**1,383,040**
Apparel uses, total	**162,100**	**85**	**137,399**	**24,701**
Men's, youths', and boys'	**106,341**	**92**	**97,328**	**9,013**
Gloves, work	41,051	83	33,976	7,075
Hosiery, work	8,149	80	6,519	1,630
Overalls & coveralls	57,141	99	56,833	308
Children's & infants'	**55,759**	**72**	**40,071**	**15,688**
Gloves & mittens	**414**	**15**	**62**	**352**
Hosiery	**12,263**	**77**	**9,497**	**2,766**
Anklets	5,785	83	4,814	971
$\frac{3}{4}$–$\frac{7}{8}$ lengths	1,296	64	829	467
Golf	180	74	133	47
Ribbed	21	65	14	7
Socks	4,981	74	3,707	1,274
Overalls, coveralls, and jeans	**29,757**	**98**	**29,031**	**726**
Knit	2,225	90	1,996	229
Woven	27,532	98	27,035	497
Sweaters, jerseys, and pullovers	**13,325**	**11**	**1,481**	**11,844**
Household uses, total	**737,335**	**34**	**253,537**	**483,798**
Drapery and upholstery fabrics	**252,198**	**61**	**153,462**	**98,736**
Rugs and carpets	**479,453**	**20**	**94,436**	**385,017**
Tufted	**258,673**	**27**	**70,150**	**188,523**
Backing fabric	78,302	32	25,057	53,245
Yarn	180,371	25	45,093	135,278
Woven	**220,780**	**11**	**24,286**	**196,494**
Thread, home sewing	**5,684**	**99**	**5,639**	**45**
Industrial uses, total	**1,305,952**	**33**	**431,411**	**874,541**
Abrasives	**32,320**	**39**	**12,340**	**19,980**
Buffing and polishing wheels	5,736	90	5,162	574
Coated	26,584	27	7,178	19,406
Automobile	**158,029**	**32**	**50,155**	**107,874**
Covers, seat	63,926	17	10,886	53,040
Linings and upholstery	90,101	38	35,393	54,708
Tops, convertible	4,002	97	3,876	126
Awnings	**21,713**	**95**	**20,627**	**1,086**
Bags	**554,505**	**13**	**70,395**	**484,110**
Belts, machinery	**43,721**	**71**	**30,961**	**12,760**
Book bindings (excluding paper)	**13,756**	**100**	**13,756**	—
Filter cloth	**6,293**	**73**	**4,594**	**1,699**
Fishing supplies	**9,188**	**67**	**6,133**	**3,055**
Flags	**2,510**	**80**	**2,008**	**502**
Hose	**37,648**	**54**	**20,324**	**17,324**
Fire	5,767	76	4,383	1,384
Other	31,881	50	15,941	15,940
Industrial thread	**56,851**	**93**	**52,808**	**4,043**
Laundry and dry cleaning supplies	**66,946**	**43**	**28,603**	**38,343**
Flat work ironer material	28,404	43	12,242	16,162
Press materials	31,879	45	14,362	17,517
Wash nets	6,663	30	1,999	4,664
Luggage coverings	**24,696**	**25**	**6,174**	**18,522**
Mail bags, U. S. Government	**3,772**	**100**	**3,772**	—
Regular	3,772	100	3,772	—
Air Mail	—	—	—	—
Papermakers' felts	**9,918**	**32**	**3,174**	**6,744**

* Source: Quantity estimates based on "Cotton Counts Its Customers," National Cotton Council (1958). Relative importance of resistance to abrasion based on ratings set forth in "Consumer Quality Requirements for Cotton Products," Frank A. McCord, National Cotton Council (1959).

TABLE I. Relative Importance of Abrasion Resistance by End Uses (Continued)

	Gross wt. of fabric & yarn (1,000 lb. cotton equiv.)	Percent cotton	Cotton (1,000 lb.)	Other materials (1,000 lb. cotton equiv.)
Pick sacks, cotton	**4,910**	**100**	**4,910**	—
Ribbons for office machines	**861**	**74**	**637**	**224**
Shoes	**229,117**	**33**	**75,514**	**153,603**
Leather	205,486	25	52,036	153,450
Rubber	23,631	99	23,478	153
Tarpaulins	**29,198**	**84**	**24,526**	**4,672**
PART B: Consumption of Materials in Uses in Which Abrasion Resistance is an Important Consideration				
Total	**1,011,735**	**65**	**656,876**	**354,859**
Apparel uses, total	**472,100**	**85**	**382,325**	**89,775**
Men's, youths', and boys'	**422,572**	**79**	**334,861**	**87,711**
Coats and jackets	**69,033**	**44**	**30,047**	**38,986**
Blanket and sheeplined	59,546	49	29,592	29,954
Mackinaws and meltons	9,487	5	455	9,032
Hosiery	**55,106**	**64**	**35,400**	**19,706**
Anklets	5,143	66	3,374	1,769
Athletic	4,482	25	1,121	3,361
Crew	2,908	95	2,763	145
Full-fashion, half-hose	16	73	12	4
Seamless, half-hose	5,842	73	4,265	1,577
Slack	36,715	65	23,865	12,850
Sweaters	**27,231**	**11**	**2,928**	**24,303**
Trousers, work	**264,215**	**98**	**259,569**	**4,646**
Dungarees	128,945	98	126,565	2,380
Other	135,270	98	133,004	2,266
Washable service apparel	**6,987**	**99**	**6,917**	**70**
Work aprons, industrial	6,987	99	6,917	70
Women's, misses', and juniors'	**2,372**	**90**	**2,128**	**244**
Gloves, work	2,197	89	1,955	242
Overalls and coveralls	175	99	173	2
Children's and infants'	**47,156**	**96**	**45,336**	**1,820**
Diapers†	**33,669**	**100**	**33,669**	—
Sportswear	**13,487**	**87**	**11,667**	**1,820**
Slacks	12,449	90	11,165	1,284
Slack suits	1,038	48	502	536
Household uses, total	**212,720**	**92**	**196,506**	**16,214**
Bed ticking	**41,550**	**80**	**33,240**	**8,310**
Towels and toweling	**171,170**	**95**	**163,266**	**7,904**
Woven	166,741	95	158,837	7,904
Knit	4,429	100	4,429	—
Industrial uses, total	**326,915**	**24**	**78,045**	**248,870‡**
Cordage and twine	**282,917**	**13**	**36,065**	**246,852‡**
Cordage	98,332	12	11,661	86,671‡
Twine	184,585	13	24,404	160,181‡
Sporting equipment	**2,559**	**77**	**1,970**	**589**
Tents	**21,854**	**100**	**21,854**	—
Wiping cloth	**10,761**	**90**	**9,685**	**1,076**
Zipper tape	**8,824**	**96**	**8,471**	**353**
PART C: Consumption of Materials in Uses in Which Abrasion Resistance is a Consideration				
Total	**1,210,803**	**51**	**613,237**	**597,566**
Apparel uses, total	**833,483**	**42**	**351,742**	**481,741**
Men's, youths', and boys'	**385,778**	**44**	**168,305**	**217,473**
Coats and jackets	**79,193**	**24**	**19,290**	**59,903**
Topcoats, overcoats, and storm coats	22,346	2	441	21,905

† Excludes diapers and diaper liners made from paper and/or non-woven fabrics.
‡ Other fibers include cotton waste in cordage and twine.

TABLE I. Relative Importance of Abrasion Resistance by End Uses (Continued)

	Gross wt. of fabric & yarn (1,000 lb. cotton equiv.)	Percent cotton	Cotton (1,000 lb.)	Other materials (1,000 lb. cotton equiv.)
Sport and leisure	25,192	15	3,804	21,388
Other jackets	31,655	47	15,045	16,610
Gloves, dress and semi-dress	**2,224**	**21**	**463**	**1,761**
Rainwear	**13,533**	**61**	**8,255**	**5,278**
Shirts, work	**51,479**	**98**	**50,488**	**991**
Suits	**75,652**	**8**	**6,841**	**68,811**
Summer	13,704	16	2,427	11,277
Winter	61,948	6	4,414	57,534
Trousers	**149,250**	**47**	**69,369**	**79,881**
Dress and sport	149,250	47	69,369	79,881
Washable service apparel	**14,447**	**94**	**13,599**	**848**
Bakers', cooks', and barbers'	9,035	96	8,674	361
Medical and hospital	5,412	91	4,925	487
Women's, misses', and juniors'	**334,750**	**32**	**105,797**	**228,953**
Coats and jackets	**87,671**	**9**	**7,593**	**80,078**
Coats	76,432	2	1,897	74,535
Jackets	11,239	51	5,696	5,543
Hosiery	**84,355**	**9**	**7,388**	**76,967**
Anklets	7,472	69	5,156	2,316
Full-fashioned	46,318	—	—	46,318
Seamless	29,393	5	1,470	27,923
Ribbed	1,172	65	762	410
Rainwear	**15,762**	**32**	**4,961**	**10,801**
Sportswear	**95,279**	**88**	**83,540**	**11,739**
Dungarees and jeans	14,539	99	14,394	145
Playsuits, sun suits, shorts, halters	50,765	94	47,719	3,046
Polo, "T", basque shirts	9,065	90	8,159	906
Slacks	20,308	64	12,997	7,311
Slack suits	602	45	271	331
Sweaters and jerseys	**51,683**	**4**	**2,315**	**49,368**
Coat and cardigan	25,464	6	1,528	23,936
Pullover and jersey	26,219	3	787	25,432
Children's and infants'	**112,955**	**69**	**77,640**	**35,315**
Coats, leggings, legging sets, jackets, ski and snow suits and pants	**33,405**	**23**	**7,809**	**25,596**
Coats	14,681	3	483	14,198
Leggings and legging sets	5,119	8	433	4,686
Jackets	6,441	69	4,440	2,001
Ski and snow suits	6,696	35	2,331	4,365
Ski and snow pants	468	26	122	346
Rainwear	**3,386**	**48**	**1,602**	**1,784**
Sportswear	**61,712**	**97**	**59,804**	**1,908**
Playsuits, sun suits, shorts	50,812	97	49,194	1,618
Polo, "T", and basque shirts	10,900	97	10,610	290
Suits and skirts	**14,452**	**58**	**8,425**	**6,027**
Skirts	6,403	48	3,058	3,345
Suits, excluding ski and snow	2,835	36	1,056	1,779
Wash suits	5,214	83	4,311	903
Household uses, total	**238,129**	**94**	**224,930**	**13,199**
Mattress covers	**3,554**	**92**	**3,270**	**284**
Oil cloth	**4,154**	**100**	**4,154**	—
Pads, quilted	**7,349**	**94**	**6,908**	**441**
Sheets	**195,182**	**99**	**194,538**	**644**
Slip covers, furniture	**11,978**	**65**	**7,786**	**4,192**
Window shades	**15,912**	**52**	**8,274**	**7,638**
Industrial uses, total	**139,191**	**26**	**36,565**	**102,626**
Carriages, baby	**533**	**80**	**427**	**106**
Friction tape	**5,001**	**80**	**4,001**	**1,000**
Insulation, electrical	**130,166**	**23**	**29,938**	**100,228**
Venetian blind tape	**3,491**	**63**	**2,199**	**1,292**

for more than 90% of annual cotton consumption in the United States provide a basis for classifying textile uses into four broad groups according to the importance which consumers attach to abrasion resistance.[3] The first group is composed of those uses in which abrasion resistance is recognized as a major quality consideration. The second group contains those uses in which abrasion resistance is identified as an important quality but not as a major quality consideration. The third group consists of uses in which abrasion resistance is recognized as a quality consideration, but not identified either as a major or important quality. The fourth group represents uses in which abrasion resistance is not separately identified by consumers as a quality consideration even though a minimum level of abrasion resistance is known to be essential for satisfactory performance.

Table I details the uses falling into the first three classifications and presents statistics on the volume of cotton and other materials consumed in each use. All uses not included in the three classifications fall into the fourth category, in which consumers do not identify abrasion resistance as a separate quality consideration.

Table II summarizes the data in Table I.

Table III presents a further breakdown of the data in Table I, indicating that consumers consider abrasion resistance to be most important in industrial and household outlets for textiles.

Table IV lists those uses in which consumers believe a significant improvement in abrasion resistance relative to other materials would strengthen cotton's position, provided other desirable qualities were not adversely affected and that price relationships with competing materials were not thrown out of balance.

Table V, a summary of Table IV, indicates that improvements in abrasion resistance would strengthen cotton's position in applications accounting for 1.38 billion pounds of textiles annually, of which 0.76 billion pounds are cotton and 0.62 billion pounds are competing materials. Thus, improvements in abrasion resistance would strengthen cotton against competitive losses in current markets totaling approximately 0.76 billion pounds yearly and at the same time provide an opportunity for cotton to achieve gains against other materials equal to about 0.62 billion pounds yearly. The data show further that the biggest opportunities for strengthening cotton in existing markets are in men's apparel items and among work clothing uses, whereas the biggest gain potentials appear to be in industrial applications. While abrasion resistance is important in many of the other apparel and household uses, cotton's position on abrasion resistance is relatively strong in most of these uses.

The market potential for a method or process which would significantly improve abrasion resist-

[3] *Consumer Quality Requirements for Cotton Products*, Frank A. McCord, National Cotton Council, 1959 (unpublished).

TABLE II. Significance of Abrasion Resistance by Degree of Importance *

(1000 lb. cotton equivalent)

	Total consumption, all materials	Cotton	Other materials
A major consideration	2,205,387	822,347	1,383,040
An important consideration	1,011,735	656,876	354,859
A consideration	1,210,803	613,237	597,566
Total	4,427,925	2,092,460	2,335,465

* Summarized from Table I.

TABLE III. Relative Importance of Abrasion Resistance by Major Use Classifications *

(1000 lb. cotton equivalents)

	A major consideration			An important consideration			A consideration		
	Total	Cotton	Other	Total	Cotton	Other	Total	Cotton	Other
Apparel	**162,100**	**137,399**	**24,701**	**472,100**	**382,325**	**89,775**	**833,483**	**351,742**	**481,741**
Men's and boys'	106,341	97,328	9,013	422,572	334,861	87,711	385,778	168,305	217,473
Women's and misses'	—	—	—	2,372	2,128	244	334,750	105,797	228,953
Children's and infants'	55,759	40,071	15,688	47,156	45,336	1,820	112,955	77,640	35,315
Household	**737,335**	**253,537**	**483,798**	**212,720**	**196,506**	**16,214**	**238,129**	**224,930**	**13,199**
Industrial	**1,305,952**	**431,411**	**874,541**	**326,915**	**78,045**	**248,870**	**139,191**	**36,565**	**102,626**
Total	2,205,387	822,347	1,383,040	1,011,735	656,876	354,859	1,210,803	613,237	597,566

* Summarized from Table I.

TABLE IV. Uses in Which Improvements in Abrasion Resistance Would Strengthen Cotton's Competitive Position [a]

	Gross wt. of fabric and yarn (1000 lb. cotton equiv.)	Percent cotton	Cotton (1000 lb.)	Other materials (1000 lb. cotton equiv.)
Total	**1,378,324**	**55**	**763,292**	**615,032**
Apparel uses, total	**491,275**	**90**	**443,608**	**47,667**
Men's, youths', and boys'	**398,278**	**92**	**364,495**	**33,783**
Gloves, work	**41,051**	**83**	**33,976**	**7,075**
Hosiery	**63,255**	**66**	**41,919**	**21,336**
Anklets	5,143	66	3,374	1,769
Athletic	4,482	25	1,121	3,361
Crew	2,908	95	2,763	145
Full-fashion, half-hose	16	73	12	4
Seamless, half-hose	5,842	73	4,265	1,577
Slack	36,715	65	23,865	12,850
Work	8,149	80	6,519	1,630
Overalls and coveralls	**29,757**	**98**	**29,031**	**726**
Trousers, work	**264,215**	**98**	**259,569**	**4,646**
Dungarees	128,945	98	126,565	2,380
Other	135,270	98	133,004	2,266
Women's, misses', and juniors'	**24,383**	**89**	**21,678**	**2,705**
Gloves, work	2,197	89	1,955	242
Hosiery—anklets	7,472	69	5,156	2,316
Overalls and coveralls	175	99	173	2
Sportswear—dungarees and jeans	14,539	99	14,394	145
Children's and infants'	**68,614**	**84**	**57,435**	**11,179**
Hosiery	**12,263**	**77**	**9,497**	**2,766**
Anklets	5,785	83	4,814	971

ance of textiles is the gross equivalent of some 4.43 billion pounds of textiles annually. A realistic potential, however, may be less than half of this total, because existing abrasion resistance qualities are adequate to satisfy requirements in many uses. Furthermore, the practical potential for a specific method or process will depend on the degree of improvement in abrasion resistance, on the cost, the effects on other qualities, and on the effectiveness with which the improvement is merchandised to the trade and to consumers. Some of the important competitive factors which must be considered in establishing demand potentials for a specific improvement in abrasion resistance are summarized in Table VI.

References for marketing data are given in Table VII.

Nature of Abrasive Wear

The terms "abrasion" and "wear" have been used interchangeably over the years to refer to the mechanical destruction of textiles both in the laboratory and in actual service use. The terms are not synonymous, and a distinction should be made between them.

"Abrasion" means a rubbing action involving relative motion between one material and another. "Wear" is a much broader term than abrasion and refers to the effects of all types of deteriorating action. The factors contributing to textile wear can be classified as either mechanical or chemical in nature. Mechanical wear includes both the gradual deterioration resulting from abrasion and tensile stressing as well as the accidental causes of failure such as rips or cuts. Chemical wear results from such actions as microbial attack, chlorine damage during laundering, sunlight degradation, and effects of strong acids. Abrasion is, therefore, only one of several factors contributing to wear.

Wear life of textiles is complicated not only by the many different factors involved but also because the relative importance of each differs greatly with end use. In apparel items, additional complications arise as a result of the occupation and habits of the wearer. For instance, the desk worker who has a habit of rolling up his shirt sleeves will find less abrasive wear at the elbows than the man who keeps his shirt cuffs buttoned. Tensile stress is a more important factor in items such as sporting apparel, where body motions cause frequent stretching. On

TABLE IV. Uses in Which Improvements in Abrasion Resistance Would Strengthen Cotton's Competitive Position (Continued)

	Gross wt. of fabric and yarn (1000 lb. cotton equiv.)	Percent cotton	Cotton (1000 lb.)	Other materials (1000 lb. cotton equiv.)
Children's ½'s and ⅓'s	1,296	64	829	467
Golf	180	74	133	47
Ribbed	21	65	14	7
Socks	4,981	74	3,707	1,274
Overalls, coveralls, dungarees, and jeans	**29,757**	**98**	**29,031**	**726**
Knit	2,225	90	1,996	229
Woven	27,532	98	27,035	497
Sportswear	**20,910**	**63**	**13,268**	**7,642**
Slacks	20,308	64	12,997	7,311
Slack suits	602	45	271	331
Household uses, total	**5,684**	**99**	**5,639**	**45**
Thread	5,684	99	5,639	45
Industrial uses, total	**881,365**	**36**	**314,045**	**567,320**
Automobile	**158,029**	**32**	**50,155**	**107,874**
Covers, seat	63,926	17	10,886	53,040
Linings and upholstery	90,101	38	35,393	54,708
Tops, convertible	4,002	97	3,876	126
Awnings	**21,713**	**95**	**20,627**	**1,086**
Belts, machinery	**43,721**	**71**	**30,961**	**12,760**
Cordage and twine	**282,917**	**13**	**36,065**	**246,852**
Cordage	98,332	12	11,661	86,671
Twine	184,585	13	24,404	160,181
Filter cloth	**6,293**	**73**	**4,594**	**1,699**
Fishing supplies	**9,188**	**67**	**6,133**	**3,055**
Flags	**2,510**	**80**	**2,008**	**502**
Hose	**37,648**	**54**	**20,324**	**17,324**
Fire	5,767	76	4,383	1,384
Other	31,881	50	15,941	15,940
Industrial thread	**56,851**	**93**	**52,808**	**4,043**
Luggage coverings	**24,696**	**25**	**6,174**	**18,522**
Mail bags, U. S. Government	**3,772**	**100**	**3,772**	—
Pick sacks, cotton	**4,910**	**100**	**4,910**	—
Shoes	**229,117**	**33**	**75,514**	**153,603**
Leather	205,486	25	52,036	153,450
Rubber	23,631	99	23,478	153

* Source: Quantity estimates based on "Cotton Counts Its Customers" (1958). Uses in which improvements in abrasion resistance would strengthen cotton's competitive position drawn from data in "Consumer Quality Requirements for Cotton Products," Frank A. McCord, National Cotton Council (1959).

the other hand, sunlight degradation and microbial attack are major factors in the wear life of awnings, tarpaulins, and similar articles used outdoors.

Textile wear is a complex process involving a wide variety of different mechanical and chemical actions. However, studies have shown relatively few uses in which deterioration is mainly chemical [32]. Although for most end uses the relative importance of all the factors contributing to mechanical wear have not been determined, salvage studies of service-worn textiles have shown that abrasive wear is a major cause of failure [32, 164].

Abrasive wear is defined for this study as the physical destruction of fibers, yarns, and fabrics

TABLE V. Summary of Uses in which Improvements in Abrasion Resistance Would Strengthen Cotton's Competitive Position *

(1000 lb. cotton equivalents)

	Total, all materials	Cotton	Other
Apparel	**491,275**	**443,608**	**47,667**
Men's and boys'	398,278	364,495	33,783
Women's and misses'	24,383	21,678	2,705
Children's and infants'	68,614	57,435	11,179
Household	**5,684**	**5,639**	**45**
Industrial	**881,365**	**314,045**	**567,320**
Total	**1,378,324**	**763,292**	**615,032**

* Summarized from Table IV.

TABLE VI. Competitive Factors in End Uses in Which Improvements in Abrasion Resistance Would Strengthen Cotton's Position *

End use	Principal quality requirements	Major competitors	Basis of competition	Price relationship with cotton
Apparel				
Men's, youths', and boys'				
Gloves, work	Low bulk; nonirritating; resistant to chemicals, fire, seam slippage; warmth; water repellent	Leather Nylon	Durability, prestige Blended with cotton for durability and sales appeal	Both leather and nylon more expensive than cotton
Hosiery	Absorbency; dimensional stability; elasticity; fast colors; luster; nonirritating; quick drying; resistant to odors, snagging, and staining; warmth; washability	Nylon Orlon Wool Rayon All types of blends	Durability, appearance, quick drying, fit Bulk, softness, quick drying, appearance Warmth, softness, prestige Price, appearance Fit, appearance, etc.	Nylon, Orlon,† wool, and blends are more expensive than cotton; rayon is less expensive than cotton
Overalls and coveralls	Dimensional stability, fast colors, no ironing, nonirritating, resistance to seam slippage, washability	Nylon blended with cotton	Durability and sales appeal	Blended nylon-cotton fabrics more expensive than all-cotton
Trousers				
Dungarees and other	Dimensional stability, fast colors, no ironing, nonirritating, resistance to seam slippage, washability	Nylon blended with cotton	Durability and sales appeal	Blended nylon-cotton fabrics more expensive than all-cotton
Women's, misses', and juniors'				
Gloves, work	Fast colors, low bulk, nonirritating, resistance to seam slippage, warmth, water repellent	Leather Nylon	Durability and prestige Blended with cotton for durability and sales appeal	Both leather and nylon more expensive than cotton
Hosiery, anklets	Absorbency, dimensional stability, elasticity, fast colors, luster, nonirritating, quick drying, resistance to odors and staining, soft colors, washability	Nylon Orlon Rayon	Durability, appearance, quick drying, fit Bulk, softness, quick drying, appearance Appearance and price	Both nylon and Orlon more expensive than cotton; rayon less expensive than cotton
Overalls, coveralls, dungarees and jeans	Dimensional stability, fast colors, no ironing, nonirritating, resistance to seam slippage, washability	Nylon in blends with cotton	Durability and sales appeal	Blended nylon and cotton fabrics more expensive than all-cotton
Children's and infants'				
Hosiery	Absorbency, fast colors, luster, nonirritating, quick drying, washability, warmth	Nylon Rayon Orlon	Durability, appearance, quick drying, fit Appearance and price Bulk, softness, quick drying, appearance	Nylon and Orlon more expensive than cotton; rayon less expensive
Overalls and coveralls	Absorbency, dimensional stability, fast colors, nonirritating, resistance to seam slippage, washability	Nylon in blends with cotton	Durability and sales appeal	Blended nylon-cotton fabrics more expensive than all-cotton
Slacks and slack suits	Absorbency, coolness, dimensional stability, fast colors, luster, no ironing, nonirritating, resistance to seam slippage, warmth, washability	Dacron Rayon Wool	Appearance and sales appeal Appearance and price Warmth and prestige	Dacron† and wool more expensive than cotton; rayon less expensive than cotton

* Source: "Consumer Quality Requirements for Cotton Products," "Cotton Counts Its Customers," and other consumer and industry surveys and studies of the National Cotton Council and other allied groups (see Table VII for complete list).

† Du Pont trademark.

TABLE VI. Competitive Factors in End Uses in Which Improvements in Abrasion Resistance Would Strengthen Cotton's Position * (Continued)

End use	Principal quality requirements	Major competitors	Basis of competition	Price relationship with cotton
Household				
Thread	Fast colors, low bulk, luster, soft colors, strength, washability	Nylon	Strength	Nylon, Dacron, silk more expensive than cotton; rayon less expensive than cotton
		Dacron	Strength	
		Silk	Strength and appearance	
		Rayon	Appearance	
Industrial				
Automobile				
Covers, seat	Absorbency; adhesive qualities; coolness; dimensional stability; fast colors; resistance to seam slippage, snagging, soiling, static electricity, staining; slipperiness; soft colors	Plastics	Durability and appearance	Plastics and nylon more expensive than cotton; rayon and paper less expensive
		Nylon	Durability and appearance	
		Paper	Price	
		Rayon	Appearance and price	
Linings and upholstery	Adhesive qualities; dimensional stability; fast colors; flex life; quick drying; resistance to chemicals, fraying, mildew, soiling, staining, and weathering; soft colors; strength; water repellent	Nylon	Appearance, durability and sales appeal	Wool and nylon more expensive than cotton; rayon and plastics competitive with cotton or lower in price
		Wool	Appearance, prestige and sales appeal	
		Rayon	Appearance and price	
		Plastics	Appearance and price	
Tops, convertible	Adhesive qualities; dimensional stability; fast colors; flex life; quick drying; resistance to chemicals, fraying, mildew, soiling, staining, and weathering; soft colors; strength; water repellent	Rayon	Appearance and sales appeal	Rayon more expensive than cotton
Awnings	Dimensional stability; fast colors; quick drying; resistance to chemicals, fire, fraying, mildew, soiling, staining, and weathering; soft colors; strength; water repellent	Metal	Durability and fixed installation	Initial cost of metal substantially higher than for cotton
Belts, machinery	Adhesive qualities; dimensional stability; elongation; flex life; lightweight; low bulk; resistance to heat, mildew; strength; water repellent	Rayon	Strength to cost	Nylon and glass fibers more expensive than cotton; rayon less expensive than cotton
		Nylon	Strength to bulk	
		Glass fiber	Strength to bulk and heat resistance	
Cordage and twine	Dimensional stability, strength, water repellent, resistance to mildew and soiling	Hard fiber	Strength and durability	Nylon more expensive than cotton; hard fibers, jute, and paper cheaper than cotton
		Nylon	Strength and durability	
		Jute	Price	
		Paper	Ease of use and price	
Filter cloth	Quick drying; strength; resistance to chemicals, heat, mildew, and staining	Nylon	Strength and durability	Nylon and Dynel more expensive than cotton; rayon and paper less expensive than cotton
		Dynel	Durability	
		Rayon	Price	
		Paper	Price and convenience	
Fishing supplies	Dimensional stability; lightweight; low bulk; quick drying; strength; resistance to chemicals, fraying, mildew, weathering	Nylon, Dacron, Silk	Low bulk, high strength, and durability	Nylon, Dacron, and silk more expensive than cotton

resulting from the contact with and relative motion of a textile surface over that of another surface. Textile materials may be rubbed against a solid surface such as dirt, wood, metal and, quite often, another textile. In addition, a fabric can abrade itself when repeatedly flexed or folded. Internal abrasion results from the relative motion and bending of the fibers and yarns over each other in the fabric structure. Damage to many textile articles in actual service probably results from a combination of direct rubbing, commonly referred to as "flat" or surface abrasion, and flexing or bending, generally termed "flex" abrasion.

Everyday examples of abrasive wear of textiles are common. Boys' wearing apparel is subject to intense rubbing throughout the normal course of playtime activity. In a similar manner, severe abrasion is suffered by the combat soldier's uniform as he crawls through an obstacle course. On the other hand, overcoat linings, upholstery fabric, and book bindings generally encounter milder attrition.

An abraded fabric will be discarded as unserviceable because of appearance or loss of mechanical properties. Fabric surfaces may become excessively fuzzy or hairy. "Pills," objectionable small balls of entangled fibers, often result from abrasion of fabrics, especially those containing high-strength synthetic fibers. Napped and pile fiber surfaces may become smooth. Shine, as on the seat of a pair of pants (particularly noticeable with wool serge), is quite common. Loss of color from crocking is occasionally a problem. Men's shirts are frequently discarded because of frayed edges at collars and cuffs.

TABLE VI. Competitive Factors in End Uses in Which Improvements in Abrasion Resistance Would Strengthen Cotton's Position * (Continued)

End use	Principal quality requirements	Major competitors	Basis of competition	Price relationship with cotton
Flags	Dimensional stability; drape; fast colors; flex life; luster; quick drying; resistance to fraying, mildew, and weathering; soft colors; strength; water repellent	Nylon	Appearance and durability	Nylon and wool more expensive than cotton; rayon cheaper than cotton
		Rayon	Appearance and price	
		Wool	Appearance and prestige	
Hose, all types	Adhesive qualities; dimensional stability; flex life; lightweight; low bulk; resistance to chemicals, fraying, mildew, and weathering; strength; waterproof	Dacron	Strength and durability	Dacron and nylon more expensive than cotton; rayon and plastic less expensive
		Nylon	Strength and durability	
		Rayon	Price	
		Plastic	Price	
Thread, industrial	Bleachability, dimensional stability, elongation, fast colors, low bulk, luster, soft colors, strength, washability	Nylon	Strength and durability	Nylon and Dacron more expensive than cotton
		Dacron	Strength and durability	
Luggage coverings	Adhesive qualities; fast colors; lightweight; low bulk; luster; resistance to mildew, scuffing, soiling, staining; soft colors; strength; water repellent	Leather	Appearance and prestige	Leather and metal more expensive than cotton; plastics and fiberboard usually cheaper than cotton
		Metal	Durability	
		Plastics	Durability and lightweight	
		Fiberboard	Low cost	
Mail bags	Lightweight; low bulk; quick drying; strength; water repellent; resistance to mildew, soiling, and staining	Paper	Low cost and convenience	Paper less expensive than cotton
Pick sacks	Dimensional stability; resistance to mildew, snagging, and weathering; strength	None	—	—
Shoes	Absorbency; adhesive qualities; dimensional stability; fast colors; flex life; nonirritating; resistance to mildew, odors, scuffing, soiling; water repellent	Leather	Appearance, durability, and prestige	Leather and nylon more expensive than cotton; plastics and rayon less expensive than cotton
		Nylon	Durability	
		Plastic	Price	
		Rayon	Appearance and price	

Loss of mechanical properties, or weakening of the textile structure, is the result of removal of or damage to individual fibers. Thus, fabrics weakened by abrasion are more readily torn or ruptured during actual service than unabraded ones. It should be understood, however, that the criterion of serviceability will vary with end use. Appearance may be of major importance in certain items of wearing apparel, but maintenance of adequate strength governs serviceability in many household or industrial uses.

The three possible mechanisms contributing to the mechanical breakdown of textiles during abrasion include frictional wear, cutting, and plucking or snagging of fibers [11, 107, 124].

Common to all is the development of stress and deformation (differing in type, magnitude, and frequency of application) within fibers and yarns which eventually leads to the breakdown of the fabric structure. The stresses developed can be those in shear, tension, compression, bending, or torsion, although, as will be pointed out later, tensile stress is believed to be of major importance.

Frictional Wear

Frictional wear occurs if the surface of the abradant is relatively smooth and the fibers are firmly held in the yarn structure. This mechanism of abrasion is analogous to the sliding of smooth metal surfaces over each other. A good example of this type of attrition is the friction of yarns in metal or porcelain guides during winding, coning or beaming operations. It is likely that closely woven fabrics containing yarns of high twist are more susceptible to frictional wear than are loosely woven fabrics containing low twist yarns.

Among the several theories of friction the two

TABLE VII. References for Marketing Data

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"Cotton in the Belting Industry," Frank A. McCord and John A. McCrossan, Jr. (March 1952) *

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"Cotton in the Carded Sales Yarn Industry," Frank A. McCord and Raymond Steinbach, Jr. (August 1954) *

"Cotton in the California Apparel Industry," Bruno M. Trevino, Jr. (March 1956) *

"Cotton in Industrial Hose," Frank A. McCord and John A. McCrossan, Jr. (April 1952) *

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"Cotton Fabrics in Upholstery, Drapes, and Slip Covers" (November 1958) *

"The Market Potential for Carpets and Rugs," Charlie W. Russell (February 1956) *

"Cotton in the Linen Supply Industry," James T. Howell, Jr. (April 1959) *

"Cotton in the Work Clothing Industry," Charlie W. Russell (June 1959) *

"Cotton Duck," Charlie W. Russell (January 1956) *

"Cotton in Filter Fabrics," Charlie W. Russell (January 1957) *

"Cotton in Industrial Tapes," Charlie W. Russell (May 1957) *

"Cotton in the Work Glove Industry," Joseph L. Williams (October 1957)*

"Fabrics and Fibers for Passenger Cars" (April 1957) †

"Women's Preferences among Selected Textile Products" (December 1957) †

"Women's Attitudes toward Wool and Other Fibers" (February 1957) †

"Mothers Discuss Cotton and Other Fibers in Children's Clothes" (February 1959) †

"Men's Preferences for Cotton, Wool, and Other Fibers in Selected Clothing Items" (February 1959) †

"Homemakers Appraise Cotton, Wool, and Other Fibers in Household Furnishings" (1958) †

"Teenage Girls Discuss Their Wardrobes and Their Attitudes toward Cotton and Other Fibers" (1957) †

"Fibers, Opinions and Practices among Manufacturers of Cordage and Twine" (June 1953) †

"Fibers Used in Insulated Wire and Cable" (April 1955) †

"Survey of Canvas Awning Fabricators" (April 1952) †

"Cotton in the Bedspread Industry," Frank A. McCord and John A. McCrossan, Jr. (December 1950) *

"Cotton in the Knitting Industry," Frank A. McCord, Raymond Steinbach, Jr., and George S. Buck, Jr. (December 1948) *

"Cotton in the Laundry Industry," Frank A. McCord and Raymond Steinbach, Jr. (December 1949) *

"Cotton in the Luggage Industry," Frank A. McCord and Raymond Steinbach, Jr. (May 1950) *

"Crease Resistance and Cotton," George S. Buck, Jr., and Frank A. McCord (April 1949) *

"The Demand for Extra-Long Staple Cotton" (December 1953) *

"Luster and Cotton," George S. Buck, Jr. and Frank A. McCord (November 1949) *

"Plastic Wall Covering and Upholstery Survey," *Architectural Record*, F. W. Dodge Corporation, New York, N. Y. (April 1953)

"Cotton's Competitive Position in Selected Industrial Items, 1958" (April 1959) *

"Cotton Quality Study. III: Resistance to Soiling," Nelson F. Getchell and Frank A. McCord (February 1955) *

* Utilization Research Division, National Cotton Council of America, Memphis, Tennessee.

† Agricultural Marketing Service, United States Department of Agriculture, Washington, D. C.

most widely considered have been the "surface roughness" and the "adhesion" theories [11, 19, 30, 121, 125, 138, 172]. Most present-day authorities agree that molecular adhesion plays the principal role in frictional phenomena, but other investigators have attributed friction to the ploughing of soft surfaces by harder ones, and to electrical forces [121].

Surface roughness. Surface roughness results from the irregular hill and valley pattern on the surfaces of all solid bodies. When two surfaces are in contact, the hills of the upper surface (for our discussion, the abradant) must move up and over the ridges of the lower or fiber surface. The force needed to lift these weights up the slope of the hills is a measure of the frictional force. This theory has been abandoned by many, since it has been found that surface roughness does not vary systematically with frictional force [11]. While experiments have shown that surface roughness accounts for only a small part of total frictional work, the destruction of fiber surfaces due to the shearing of minute surface irregularities as a result of mechanical interlocking with the hills or ridges of abradant surfaces is quite conceivable [172].

Adhesion. The more generally accepted adhesion theory suggests that molecular forces between two solid surfaces in close contact act as "molecular welds" at the junction. The shear force needed to separate these junctions is a measure of the frictional force. It has been suggested that sufficiently strong adhesion will cause shear of the fiber itself rather than of the junction [30]. This would result in fiber destruction as a consequence of friction. On the other hand, should adhesion be weak, shear may occur at the interface rather than in the bulk of the fiber. In this instance, fiber wear would not occur although frictional effects were present.

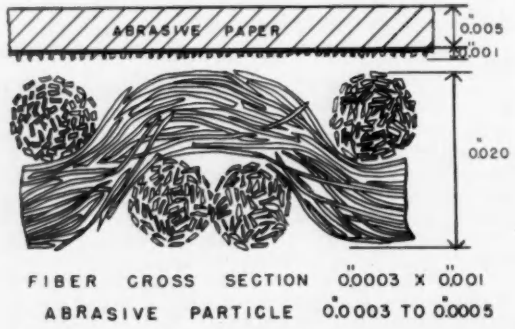

Fig. 1. Schematic cross section of cotton fabric and abrasive paper.

In addition to damage directly caused by removal of fiber particles, frictional forces can destroy textile structures by other, indirect means. To illustrate, consider two different yarns. In the first, assume that twist and interfiber friction are such that cohesive forces holding fibers together in the yarn are very strong. In the second, assume that the same cohesive forces are relatively weak. In the first, frictional forces developed should be dissipated largely in the fibers by development of tensile or other stress and by removal of fiber particles. Repetition of such stresses results in fiber fatigue (loss of fiber mechanical properties), leading to rupture. It is even possible that, on first contact, frictional force may be sufficiently high to rupture the fiber. When fiber cohesion is relatively poor, however, as in the second yarn, frictional force can displace or remove fibers from their normal position in the yarn. Thus, breakdown of the structure occurs without appreciable fiber damage.

A more complex situation is apparent when a condition intermediate between the above two cases is present. In such circumstances, cohesive forces tending to maintain the fibers in the yarn and those forces holding the fiber itself intact will operate together to resist frictional force.

Frictional heat developed during abrasion may also cause damage, particularly if the fiber is thermoplastic or heat sensitive. Melting of nylon parachute fabric has been reported due to the rapid relative motion of the fabric as it unfolded out of the carrier bag. Damage resulting from heat effects of friction is believed to be extremely small, however, in ordinary textile applications.

Cutting

Fibers will be cut if abradant surface areas are very small and sharp compared to that of the fiber. Fine abrasives, such as emery paper and sandpaper used in laboratory abrasion testing, cause a cutting action when rubbed over a fabric surface [150]. Figure 1 illustrates the relative dimensions of a cotton fabric and abrasive paper used in laboratory testing. It is easy to visualize cutting of individual fibers by the sharp surfaces of such abrasive particles. The cutting process is known to be associated with the development of complex stress patterns which can lead to fiber tensioning, bending,

Fig. 2. Loosening and mild disintegration of yarn structure resulting from abrasion of cotton fabric.

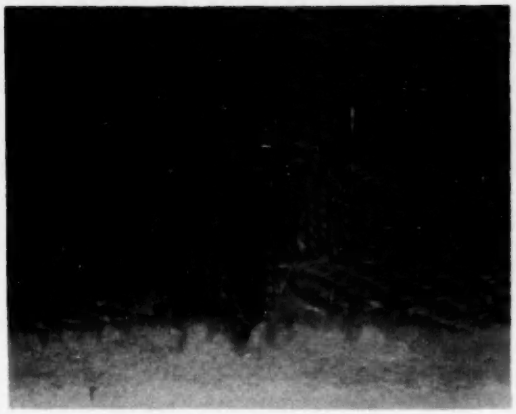

Fig. 3. Hole formation resulting from abrasion of cotton fabric.

or slippage in addition to the damage caused directly [11].

Plucking

In addition to cutting and frictional effects, plucking or snagging of fibers and yarns can take place in a manner similar to the plucking of a guitar string as the abradant traverses the fabric surface. Plucking will be more pronounced when the normal forces between the abradant and fabric are large, since deeper yarn penetration will occur. Depending upon the force exerted by the abradant and the extent to which the fiber is bound in the yarn, rupture on first contact, slippage, or repeated stressing can result. In any event, fiber life prior to rupture as a result of tensioning or bending would depend upon the magnitude and frequency of stress application

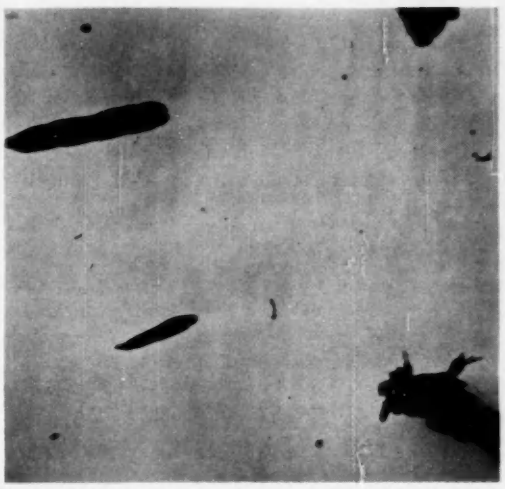

Fig. 4. Particles removed from cotton fibers during dry abrasion of canvas fabric.

and the fiber mechanical properties. Loosely woven fabrics containing low twist yarns would be more subject to abrasion damage due to plucking than tightly woven fabrics containing yarns of high twist. In the latter, fibers would be more securely bound in the yarn and therefore less accessible to the abradant.

Visual Effects of Abrasion

At the outset it is worth while to take a look at some worn fabrics which illustrate breakdown caused by abrasive wear. Figures 2 and 3 show abraded cotton fabrics worn by military personnel on an army combat course. Figure 2 shows scuffing of the fabric surface and loosening and mild disintegration of yarn structure, resulting in a hairy appearance. A more severe abrasion resulting in complete disintegration of yarn structure and hole formation is illustrated in Figure 3.

Removal of fiber particles. Sufficient evidence exists to prove that innumerable small fiber particles of various size are removed during abrasion. Abrasion testing with blade-type abradants removes particles from the cotton fiber as small as 100–200 Å [150]. Other observations have shown that particles 2 or 3μ wide and 40–50μ long are torn away from cotton fibers during actual wear [108]. In a study of the fragmentation of cotton fibers during dry abrasion [47], chiplike particles 0.15–0.50μ in diameter and from 1 to 3μ long were obtained by rubbing together two heavy pieces of canvas (see Figure 4). Wet abrasion, on the other hand, pro-

duces very long, fine fibrils 100–200 A in diameter.

Because of the inherent flexibility and ease of deformation of fibers, it is not likely that abrasive wear will occur predominantly through removal of fiber particles. Observation of fibers from worn textile articles shows that abrasion causes gross fiber damage rather than gradual wear through removal of fiber material.

Fig. 5. Wool fiber from wool/cotton nightgown showing abrasion with fibrillation.

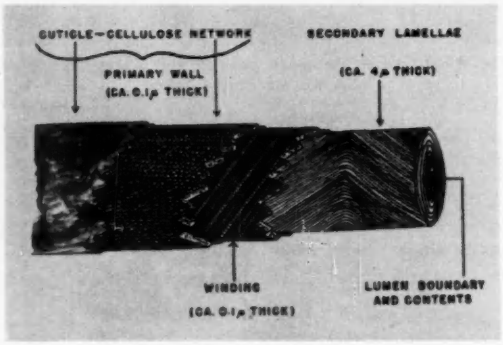

Fig. 6. Schematic diagram of cotton fiber structure.

Fig. 7. Cotton fibers from worn collar showing abrasion with fibrillation.

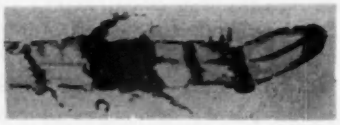

Fig. 8. Cotton fiber from worn overall showing cuticle damage.

Gross fiber damage. Microscopical examination of fibers taken from worn textile articles can be most helpful in understanding the mechanical breakdown of fabrics in service use. Clegg [32] has made an extensive and informative microscopic examination of cotton fibers taken from worn textile articles. Fibers from worn cotton shirts, overalls, pajamas, handkerchiefs, umbrellas, sheets, pillow slips, kitchen blinds, fire hose pipes, and several other articles were included in the examination. Depending upon the nature and intensity of abrasive action encountered during service use, fibrillation, cuticle damage, and transverse cracking were typical forms of cotton fiber damage observed. Staple diagrams of fibers taken from warp and filling yarns of a worn shirt showed considerable breaking of fibers. Breaking load measurements also showed a reduction to less than half that of the original strength of fibers. The strength loss was found to be largely the result of transverse cracks randomly distributed along the entire length of fibers. Fluidity figures showed that chemical deterioration was responsible for only a relatively small portion of the strength losses of cotton garments and articles except kitchen curtains, awnings, and similar fabrics, where sunlight, gas fumes, and atmospheric elements are the principal degradative agents.

Fibrillation.—Fibrillation is analogous to the splintering of wood and involves the longitudinal disintegration of the fiber into a series of elements revealing the fibrillar structure. Fibrillation is most strikingly illustrated by wool (Figure 5). Figure 6 shows the component structural layers of the cotton fiber, a feature distinguishing it from the more homogeneous structure of most synthetic fibers. The outermost layer or primary wall contains most of the noncellulosic impurities (raw cotton is about 94% pure cellulose). Secondary lamellae comprise the bulk of the cotton fiber and consist of concentric layers of fibrils or "growth layers" which spiral around the fiber axis.

In view of the fibrillar nature of cotton, as shown in Figure 6, it is not surprising that fibrillation also occurs when cotton is abraded. Figure 7 shows cotton fibers taken from a worn collar. The unruptured fiber and fiber ends manifest a fair amount of fibrillation. Examination of cotton fibers taken from worn overalls, heavy work suits, coated leggings, and gloves have shown fibrillation (similar to that depicted in Figure 7) to be the only form of

fiber damage present. It is noteworthy that all of the fabrics mentioned above have one thing in common: the fibers comprising them are firmly held in the fabric and therefore would be subject to an intense abrasive action with little individual fiber movement occurring. Fibrillation probably results largely from tensile stress due to frictional force, because the damage shown in Figure 7 closely resembles that obtained from direct tensile rupture of single cotton fibers [193].

Cuticle damage.—As shown in Figure 6, the cuticle is the outermost portion of the primary wall of the cotton fiber. Cuticle damage appears to be due to abrasion of a gentler type (Figure 8). Fibers which are not too firmly bound either by fabric structure or starching do not receive intense abrasion of the type leading to fibrillation. The bruised appearance of the fiber is attributed to a loosening, tearing, and partial or complete removal of the cuticle.

Transverse cracking.—Considerable damage to cotton fibers also results from the development of cracks at right angles to the fiber axis (Figure 9). From tensile breaks on single cotton fibers and other laminated structures, successive rupture of growth layers would more likely be expected than the appearance of cracks [11, 193]. The fact that crack formation is possible with a laminar structure when stress distribution is nonuniform suggests that considerable bending and flexing of cotton fibers occur during abrasive wear. In the bent condition, stresses acting on a fiber vary from maximum tensile on the outside curvature of the bend to compressive stresses on the inside curvature.

The fibers shown in Figure 9 were taken from the filling of a worn shirt. Since the filling was protected by the warp it did not receive surface abrasion but was subject to bending and flexing. Examination of cotton fibers from other items such as handkerchiefs and umbrella fabric showed crack formation to be the sole type of damage. Here again, internal abrasion from folding and flexing is predominant, with little exposure to surface rubbing. These observations lead to the conclusion that cracking is largely the result of repeated fiber bending and flexing. Confirmation of cracking resulting from fiber bending is also obtained from laboratory flexing of cotton fibers [184]. Figure 10 shows a photomicrograph of the point of bending of a Sea Island cotton fiber. It is seen that a crack developed in the flattened area of the bend without evidence of fibrillation. Fibers from the warp yarns of a worn shirt also showed some degree of cracking. Since these yarns were exposed to the rubbing surface, it is possible that some cracking is initiated by abrasion and then propagated by bending actions.

The cotton garments and articles included in Clegg's study indicated damage by all three factors discussed above. Items such as pajamas, dresses, trouser pockets, linings, sheets, pillow slips, and shirts, which are subject to surface abrasive wear as well as to flexing and bending, showed evidence of all three forms of fiber damage.

Factors Determining Abrasion Resistance

Abrasion damage to textiles under a given set of conditions depends on fiber mechanical properties, yarn and fabric construction, and finish.

All three factors significantly affect abrasion performance, but it is extremely difficult to assign a relative order of importance. Through faulty construction or improper application of finish, fibers with excellent mechanical properties can be made into fabrics with poor abrasion resistance. On the other hand, fibers with poor mechanical properties can be made into fabrics with adequate abrasion resistance through proper construction or choice of finish.

Fiber Mechanical Properties

Prior to World War II, most studies on the abrasion of textiles were concerned with the develop-

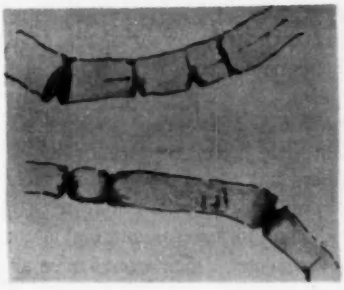

Fig. 9. Cotton fibers from filling of worn poplin shirt showing transverse cracking.

Fig. 10. Photomicrograph of Sea Island cotton fiber subjected to repeated bending.

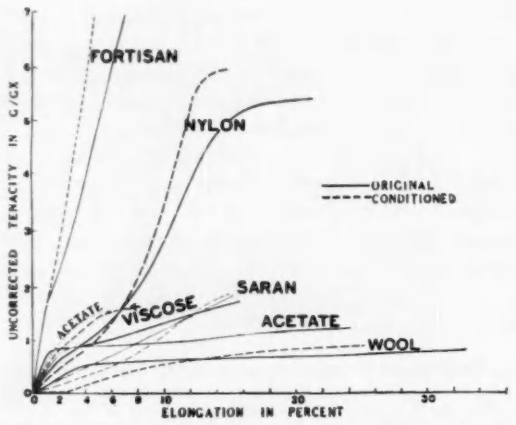

Fig. 11. Stress–strain curves of fibers before and after mechanical conditioning.

ment of testing devices and the evaluation of the resultant destruction of the materials. Very little work was done to determine the effects of fiber properties. Although a more thorough understanding of the fiber properties required for good abrasion resistance is still to be achieved, research to date has shown that mechanical properties are at least a qualitative indication of performance.

Experiments relating abrasion resistance to fiber mechanical properties have been conducted mainly on yarns to eliminate as much as possible the effects of fabric structure. Abrasion performance could thus be related more nearly to the fiber material itself. For filament yarns this procedure is particularly practical, since maintenance of yarn structure depends primarily on breakage or damage of individual filaments. However, for staple fibers such as cotton, the effects of yarn structure cannot be eliminated. Abrasion resistance of staple yarns depends not only upon rupture or damage to individual fibers but also upon factors such as twist, fiber length, and interfiber friction. Frictional force developed during abrasion is another factor which is difficult to assess but which would have an effect on abrasion resistance.

In spite of the complications arising from the above factors, laboratory abrasion studies on yarns together with limited information obtained on the abrasion performance of fabrics have shown that fiber tensile, flexural, and shear properties are important variables determining abrasion resistance. The evidence available points to tensile properties as being of major importance.

Tensile properties. Numerous studies show that abrasion resistance is higher for fibers which have a greater capacity to absorb work under conditions of repeated stretching [2, 59, 68, 174].

The work absorption of fibers during repeated stretching is measured by the area under the stress–strain curve after mechanical conditioning, that is, after nonrecoverable elongation has been removed by repeated relaxing and stretching of the fiber short of failure [175]. Depending upon fiber elasticity, work absorption after repeated stretching is always less than that obtained on first stretching. Fibers with high elasticity show little reduction in work absorption after repeated stretching, while those with poor elastic behavior exhibit large losses. Figure 11 shows stress–strain curves of several fibers before and after mechanical conditioning. For all fibers shown, the area under the stress–strain curve of the conditioned fiber is smaller than that of the fiber subjected to only one stretching. Abrasion resistance is related to the area under the broken line in Figure 11, representing work absorption of the mechanically conditioned fiber.

Capacity for work absorption during repeated stretching depends upon strength, elongation, and elasticity. Fibers which are deficient in these properties normally have poor abrasion resistance in comparison with fibers excelling in them. However, elongation and elasticity appear to be more important than strength. Glass fibers are exceptionally strong and elastic, but because of their extremely low elongation they are very readily damaged in service. The work absorption of viscose and acetate on first stretching is quite high, as shown in Figure 11. High permanent set associated with the poor elasticity of these fibers markedly reduces their work absorption after repeated stretching, however, and contributes to their relatively poor abrasion resistance. Wool, although a weak fiber, has high stretch and, like viscose and acetate, exhibits high work absorption on first extension. Because of its excellent elasticity, wool retains most of its ability to absorb work after repeated stretching; hence its abrasion resistance is quite good despite its low strength. A combination of high strength, high elongation, and excellent elasticity contributes to the marked abrasion performance of nylon.

A typical stress–strain curve for cotton before and after repeated stretching would be similar to that for conditioned acetate, shown in Figure 11, although

cotton's tenacity would be higher. Because of its comparatively low elongation, the work absorption of cotton on first stretching is low compared to most fibers. Although permanent set in cotton (*ca.* 50%) is about equal to that in viscose rayon, the absolute reduction in work absorption of cotton after repeated stretching is small compared to rayon and acetate [175].

Response of the cotton fiber to stretching forces in terms of its molecular structure and the arrangement of molecules within the fiber has been given considerable attention [25, 49, 94, 102, 112, 158]. The high order of molecular arrangement and the presence of strongly attracting hydroxyl groups (Figure 12) are responsible for the high degree of crystallinity found in cotton cellulose [183]. These groups of well-ordered molecular units or fibrils are oriented at an angle to the fiber's long axis, as shown in Figure 6. Cotton's extensibility is quite low in comparison to fibers like wool, where the existence of large, bulky side groups between molecular chains prevents formation of a well-ordered crystalline structure and allows extension of the fiber by unfolding or ordering of molecular chains along the fiber axis [158].

When the cotton fiber is extended, the angle of fibrillar orientation is decreased and the fibrils are aligned more nearly parallel to the fiber's long axis. The increased fibrillar orientation is possibly the net result of bond stretching, slippage between cellulose chains, slippage between fibrils, and slippage between groups of fibrils or growth layers [49]. Formation of new attractive forces resulting from relative movement between these structural elements prevents immediate restoration of the cotton fiber to its original unstretched state and contributes to permanent set. In contrast to the many cross-linkages present in the wool molecule, the absence of similar restoring forces between molecular chains in cotton further adds to its permanent set.

The abrasion performance of cotton is much better, however, than would be expected from its work absorption capacity as judged from stress–strain data. On the basis of the curves shown in Figure 11, wool should be superior to cotton while acetate and cotton should have about equal abrasion resistance. On the contrary, cotton exhibits abrasion resistance equal to or better than wool and far superior to that of acetate [10, 174].

A partial explanation might lie in the high stretch of both acetate and wool. Although work absorption on first extension is higher for both fibers than for cotton, high stretch reduces the cross-sectional area of acetate and wool so that concentrated stresses develop from small abrasive forces. This situation is particularly applicable to acetate, where a high portion of the stretch is nonrecoverable. In wool, however, concentrated stresses may not develop if the fiber is allowed to recover its original length between successive applications of abrasive force. Cotton's comparatively low stretch is, therefore, advantageous in this respect.

Evidence supporting the disadvantages of high, nonrecoverable stretch is also obtained from the abrasion performance of decrystallized cotton [177]. The initial work absorption of decrystallized cotton is considerably higher than that of untreated cotton, partly because of increased stretch obtained through a reduction in crystallinity. However, most of the increased stretch is nonrecoverable. Abrasion resistance of decrystallized cotton is considerably less than that of untreated cotton and is similar to that of spun viscose.

Further evidence of a relationship between tensile properties and abrasion resistance is provided by cottons that have been treated for wrinkle resistance. Application of thermosetting resin precondensates to cotton has enhanced its wrinkle recovery properties and dimensional stability. However, in accelerated laboratory testing, treated cottons show considerable loss in abrasion resistance. Even greater losses are noted in testing resin-treated viscose rayon.

It has been conclusively shown that the reduction in laboratory abrasion resistance accompanying resin treatment of cellulosic fabrics is mainly the result of changes in stress–strain properties of fibers. When the resin is properly applied, the losses are not caused by cellulose degradation [58, 59]. Although elastic recovery of the cotton fiber is increased, extensibility and strength are reduced. Consequently, the work absorption capacity of resin-treated fibers is less than that of untreated ones. Chemical cross-linking and resin deposition within fibrils, between fibrils, and between growth layers of the cotton fiber reduce relative movement between these structural elements [49, 117]. Extensibility is therefore reduced, but elastic recovery is increased since there is less tendency to form new forces of attraction resulting from movement of structural elements from their old positions. Sim-

ilarly, strength is lowered because fibrils are less free to move into more oriented positions along the fiber axis.

Increased elastic recovery of resin-treated fibers should compensate somewhat for their lowered extensibility. Although resistance to higher strains is less, ability to recover from lower ones is increased. Studies with viscose rayon have shown that the difference in laboratory abrasion resistance between resin-treated and untreated fabrics depends greatly upon the test conditions [118]. At the high loads normally used in accelerated laboratory tests, abrasion resistance of resin-treated fabrics was considerably less than that of the untreated. As the severity of the test conditions decreased, however, the difference in abrasion resistance between the two became smaller until, under very mild test conditions, abrasion resistance of resin-treated fabrics actually exceeded that of the untreated. Thus, there is evidence that while high work absorption is necessary for more severe abrasion conditions, elasticity is more important under the mild conditions more likely to be encountered during most acual wear situations.

Although studies similar to the above have not been reported for cotton, the results would probably be in the same direction. In any event, service wear performance of resin-treated cotton has not confirmed to date the markedly poorer abrasion resistance which accelerated laboratory testing indicates. When controlled service testing becomes more extensive, the results will probably confirm the suspicion that accelerated laboratory testing of resin-treated cottons does not correlate well with normal conditions of service use.

Very little systematic work has been reported on the wet abrasion performance of cotton. In addition to wet tensile properties, other factors are involved, such as fiber swelling and the lubricating action of water within fibers and between fibers and yarns. On the one hand, the increased strength of cotton when wet could enhance its abrasion resistance. A major contributing factor to the poor wet abrasion performance of viscose rayon, for example, is its low wet strength [112, 119]. The increased elongation of cotton when wet would be of little merit, however, since most of it would be nonrecoverable. On the other hand, fiber swelling could stiffen fabrics and reduce the flexibility needed to prevent development of high abrasive stresses [10]. Finally, the lubricating action of liquids might tend to increase abrasion damage resulting from fiber slippage in yarns [189].

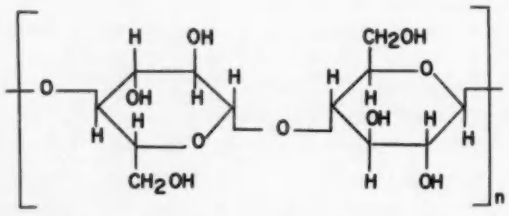

Fig. 12. Molecular structure of cotton cellulose.

Shear properties. Shear stress is the result of forces acting perpendicularly to the fiber's long axis.

The inherent flexibility and freedom of motion of fibers in a textile structure are such that stresses other than tensile should seldom develop to any appreciable magnitude [69, 126]. However, when sharp abrasive surfaces are present or fiber movement is restricted, the resistance of the fiber to shear becomes important [12]. Field service tests conducted by the Army Quartermaster Corps have indicated that an optimum balance between shear and tensile properties is desirable, depending upon the abrasion conditions [10].

Resistance to shear provides further explanation of cotton's comparatively high abrasion resistance in spite of its relatively low work absorption during repeated stretching. Authorities suggest that cotton's resistance to shear, as reflected in its excellent knot strength [148], is a major factor accounting for its low abrasion damage. The spiral structure of cotton (Figure 6) contributes to its good shear properties in that orientation of fibrils is not completely along the lengthwise direction of the fiber. While longitudinal orientation provides improved tensile strength, orientation of structural elements transverse to the fiber axis contributes to improved shear strength [119]. Abrasion studies have indicated that too much lengthwise orientation resulting from "overstretching" of fibers lowers abrasion resistance [174].

It has been suggested that the order of abrasion resistance of textile fibers can be obtained roughly by calculating the ratio of the square of shear tenacity to initial Young's modulus. Such ratios computed for nylon, cotton, viscose, and acetate have shown a marked resemblance to the order of abrasion resistance of these fibers [10].

Flexural properties. Bending resistance of fibers and tensile stress developed from interfiber friction are important factors determining internal abrasion damage resulting from fabric flexing [9]. Quartermaster tests on the flexing performance of nylon and wool flags indicate the importance of interfiber friction [11]. Since bending resistance of nylon and wool are comparable, equal performance might have been expected if the effects of interfiber friction were negligible. Blending of nylon with the wool markedly improved the flex life of the flags, however, indicating the development of high tensile stress resulting from interfiber friction. Improvements in fabric flex abrasion resistance from the use of lubricants also indicates the contribution of interfiber friction [5, 42, 55].

Fiber bending creates tensile strain on the outside curvature of the bend and compression on the inside [58]. Since buckling occurs readily, the net result is that tensile strain is high, while compression is believed to be relatively small [69]. Thus, fibers with high elastic extensibility show good bending resistance so that the order of inherent abrasion resistance might be somewhat similar to that for flexing endurance. Reported values for the bending resistance of some fibers indicate a marked similarity between the two, except for the relative positions of cotton, wool, and nylon [11]. On the basis of flexing endurance, abrasion resistance of wool should be significantly greater than that of cotton and on a par with that of nylon. Again, the discrepancy can be explained by considering the importance of other properties, such as shear strength or ultimate tensile strength.

Construction

Construction is a general term referring to gross fiber dimensions and to the manner in which fibers are arranged in a textile structure. The effects of construction on abrasion resistance have received considerably more attention than the effects of fiber mechanical properties. Most of the information available, however, relates to flat or surface abrasion. Very little systematic work has been reported on abrasion resulting from fabric flexing.

Fiber shape. Such fiber dimensions as length, fineness, surface roughness, and shape of cross section influence abrasion resistance by their effects on fiber cohesion in yarns and magnitude of stresses and strains developed by abrasive forces.

The rapid deterioration of yarn structure from removal or displacement of even a few fibers when cohesion is poor has been emphasized by several investigators [40, 107]. Longer fibers are generally more difficult to remove or displace from yarns than shorter ones. Tests have shown that filament yarns are usually more abrasion resistant than their staple counterparts [2, 78, 174]. Studies conducted by the Quartermaster Corps indicate that fabrics containing longer staple cotton have better resistance to abrasion than those containing shorter staple [128]. Although comparative data are not available, this evidence suggests that fabrics made from combed cotton yarn should be more abrasion resistant than those made from carded cotton yarn, since combing removes much of the short fiber normally present in raw cotton. In addition, longer fibers make stronger yarns at equal twist and size, so that fabrics weakened by abrasion can better withstand periodically applied stretching [127].

Although fine fibers form stronger yarns, evidence suggests that coarse fibers improve abrasive wear, within limits [77, 78, 146, 168]. Fibers which are too thin are easily ruptured, because little abrasive force is needed to develop high stresses. If fibers are too coarse, however, fracture occurs more readily on bending, because higher strains develop in the outer layers of the bend [146]. In addition, reduction in the number of fibers in the yarn cross section lowers fiber cohesion.

Some evidence exists to show that fiber cross sections which are flat, elliptical, or hollow will withstand abrasive wear better than round ones, because outer layers of round fibers must stretch over a greater distance, creating higher strains [77, 166].

Little information is available relating fiber surface roughness to abrasion performance. However, "linenizing" cotton sheeting with sulfuric acid has been reported to improve significantly actual wear life of sheets because increased smoothness reduces friction [200]. Some of the improved smoothness may be due to alterations in the fiber surface itself. It has been shown that the swelling action of sulfuric acid reduces the gross irregularities normally present on the surface of untreated cotton fibers [64]. Since mercerization also produces a smooth fabric surface, comparable improvement in wear life might be expected.

Yarn structure. Diameter.—Increased abrasion resistance with larger diameter yarns has been noted

on many occasions [78, 146, 150, 178, 194] and has been verified by accelerated service testing [204]. Heavier yarns containing more fibers than lighter ones permit better distribution of stress for a given load and, in addition, require rupture or displacement of a larger number of fibers before failure occurs. In plied yarns, however, abrasion resistance depends upon the number of plies as well as on yarn size. Tests have shown, for example, that abrasion resistance of a 2-ply yarn is roughly five times that of a singles yarn of equal count [2]. Increasing yarn ply provides the greater fiber cohesion necessary to reduce abrasion damage.

It is the thickness of yarns exposed to the rubbing surface, however, which effectively determines abrasion resistance of fabrics [13]. In sateen constructions, for example, where only one yarn system is predominantly exposed on either surface of the fabric, it is advantageous to employ coarser yarns on the surface to be exposed to abrasion but of little merit to utilize heavy yarns in the protected yarn system on the reverse side of the fabric.

Where abrasion resistance is measured solely in terms of surface appearance, heavy yarns do little good. Objectionable fuzz can accumulate just as rapidly on the surface of thick fabrics as on thin ones.

Thicker yarns may not necessarily improve flex abrasion to the same extent as flat abrasion. The larger mass to be abraded may be offset to some extent by the higher strains on fibers in the outside curvature of larger diameter yarns.

Twist.—Abrasion resistance increases with twist to an optimum value beyond which further increases in twist cause decreases in abrasion performance [13, 78, 128]. The relationship between abrasion resistance and twist is, therefore, similar to that between tenacity and twist, although there is no evidence that the optimum twist for strength and for abrasion performance are the same. Increasing twist to the optimum value improves abrasion resistance by the accompanying improvements in fiber cohesion. Thus, the removal or displacement of fibers by snagging and friction is minimized.

Twist beyond the optimum value provides no further improvement in fiber cohesion and imposes large stresses on fibers [127]. In addition, the capacity of the yarn to flatten or rotate is reduced [13]. Damage can be alleviated if fibers can yield or slip under the surface of the moving abradant. Such fiber mobility can be obtained by both rotation and flattening of yarns. Highly twisted yarns are less prone to rotation and do not flatten in compression as readily as low twist yarns. Compressive flattening also prevents damage by permitting abrasive forces to act over larger areas of yarn surface.

Fabric structure. Yarn crimp, threads per inch, and weave affect abrasion resistance, since they determine the yarn surface area exposed to rubbing, fiber cohesion in yarns, distribution of warp and filling areas exposed to abrasion (consequently the intensity of damage received by each yarn system), and mobility of yarns and fibers needed to prevent damage from the impact of abrasive forces.

Crimp.—High crimp in a given direction projects yarns in that direction to the rubbing surface. The complementary yarns, containing lower crimp, are protected [13]. Thus, highly crimped yarns suffer greater abrasion damage, while the protected yarn system suffers less. Such unbalance of crimp can result in early failure of a fabric because of the excessive damage imposed on one yarn system, particularly when applied stresses operate equally in all directions. However, should stresses developed during wear be predominant in one direction (warp or filling), protection afforded by high crimp in the opposite direction helps to preserve the life of stress-bearing yarns and thus prevents early failure.

Threads per inch.—Laboratory tests and actual wear trials have demonstrated that abrasion resistance improves with increasing threads per inch [13, 81, 150, 178]. The larger surface area exposed to rubbing permits better distribution of abrasive stresses. This same principle explains increased abrasion resistance with high pile densities and heights in carpets and high courses per inch in knit fabrics [53, 146].

Fiber binding is also improved by increasing the number of threads per inch, since more yarn intersections are available. The importance of providing adequate fiber binding is exemplified in nonwoven fabrics. Studies with plastic-bonded fiber webs have shown that breakdown can occur largely from fiber slippage, with little damage to the fibers themselves [167].

There are, however, limitations on higher fabric counts. Use of too many yarns per inch causes rigid areas with loss of fiber and yarn movement [13]. Although very tightly woven structures have improved flat abrasion resistance, damage from flex abrasion is increased considerably [29].

Weave.—Plain weaves provide better fiber binding than twills and sateens because they contain more yarn crossovers. However, when the advantages of high fabric count are desired, twills, sateens, and similar constructions give adequate binding with less loss in fiber and yarn movement than occurs with plain weaves [13].

Knowledge of service conditions is necessary to determine optimum designs for particular end uses. If abrasion and subsequent tensioning of a fabric during service are likely to occur in all directions, choice of weave should be such that warp and filling yarns are equally exposed at the rubbing surface [200]. Such an arrangement evenly distributes damage to both yarn systems.

However, when abrasion and tensile stressing during service occur predominantly in only one direction, choice of weave becomes more complicated. Two opposing factors are involved. First, yarns are damaged more from crosswise rubbing than from lengthwise abrasion [13]. Second, it is advantageous to protect the stress-bearing yarns with long floating yarns, as in sateen constructions [83]. Thus, protection of stress-bearing members is accomplished at the expense of placing protecting yarns in their most vulnerable position to abrasion damage. Figure 13 illustrates various degrees of yarn protection achieved by control of float length. Excellent protection of the warp by the long filling float of the sateen fabric is clearly shown. Since in most wear situations direction of abrasion and tensioning are the same, maximum abrasion life of a fabric is never achieved. However, in rare cases when the direction of abrasion and stress application are opposite, protection of stress-bearing yarns can be realized with minimum damage to yarns exposed to the rubbing surface.

When fabrics are abraded in one direction but receive only mild external stressing, protection of stress-bearing yarns is less important. It is then advantageous to use high fabric counts, thick yarns, and longer floats in the direction of rubbing so that

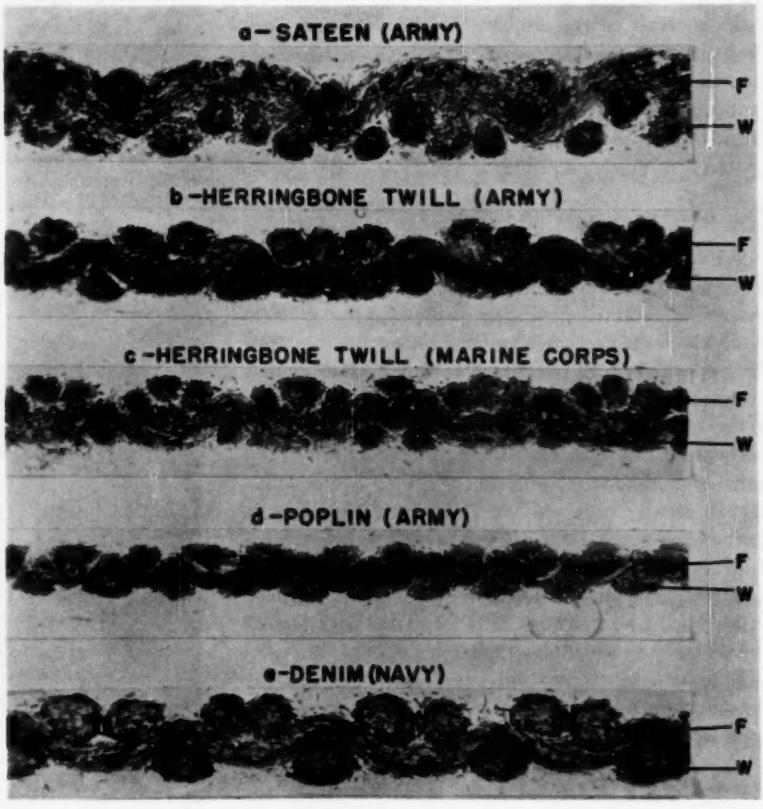

Fig. 13. Cross-sectional views of cotton fabrics.

the complementary yarns have relatively little significance. Such designs are particularly desirable if appearance is important, because they minimize fuzziness due to snagging. Crosswise abrasion of yarns enhances fiber snagging and results in a hairy appearance [13].

Finishes

Finishing agents have been applied to modify the properties of cotton as far back as the Middle Ages, when starch was first used to protect warp yarns from abrasion during weaving. Additive finishes such as starch are still in common use today, but, except for warp sizing, they are seldom applied solely to affect abrasion resistance. Additive finishes are deposited on fiber surfaces and usually alter the hand, body, and appearance of fabrics in addition to affecting functional properties such as soil resistance, tear strength, and water resistance. The use of such finishes alters abrasion characteristics in one way or another through the mechanisms of fiber binding, protection, and lubrication.

In contrast to the additive finishes, the more recent chemical finishes impart to cotton such properties as wrinkle and mildew resistance by chemical modification of the cotton cellulose itself. Such chemical modifications are also usually accompanied by changes in abrasion performance.

Finishes—Additive

Binding agents. Binding agents are polymeric materials such as starches, gums, proteins, and thermosetting and thermoplastic resins having particle sizes too large to penetrate the cotton fiber. They are deposited on fiber or yarn surfaces either as discrete particles or as films, cementing the fibers together and physically protecting them from the abradant [114, 160, 186, 195]. To be effective the agent should adhere firmly to the fiber. Better binding is usually obtained when a continuous film is formed. Figures 14 and 15 show cotton fibers from fabrics treated with thermoplastic resin latices and illustrate deposition of discrete particles in the case of the hard polymer latex and formation of a film in the case of the soft polymer latex.

Binding agents generally improve resistance to flat abrasion where damage is largely due to surface rubbing without flexing or bending [1, 67, 85, 116, 132]. In flex abrasion, where fiber or yarn bending and movement are involved in addition to surface rubbing, binding agents may be less beneficial. Although protection from surface abrasion is provided, increased interfiber friction resulting from the presence of the agent reduces fiber movement needed to prevent the development of high stresses [9]. Depending upon the degree that fiber mobility is restricted, improvement, little or no improvement, or considerable reduction in flex abrasion may be ex-

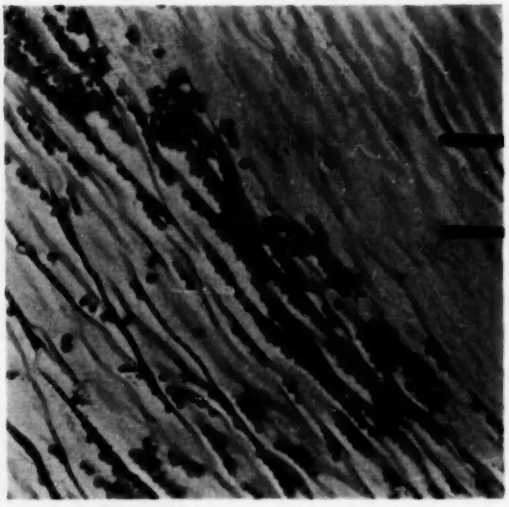

Fig. 14. Electron micrograph of surface replica of cotton fiber from fabric treated with hard acrylic polymer latex dispersion (5% pickup), polystyrene-carbon method.

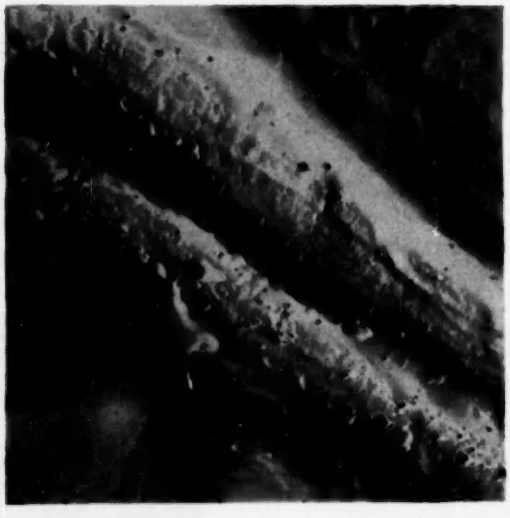

Fig. 15. Electron micrograph of surface replica of cotton fiber from fabric treated with soft acrylic polymer latex dispersion (30% pickup), polystyrene-carbon method.

pected [18, 67, 154]. Improvements in flex abrasion using a nitrile latex, for example, are believed to result from the deposition of discrete particles or lacy networks which bind cotton fibers at intervals so that movement is not completely restricted [154].

Water-soluble polymers, such as starches, gums, and proteins, will impart temporary abrasion resistance to cotton, as in the sizing of warp yarns prior to weaving, where a major cause of breakage is abrasion of warp yarns against the heddles and reed of the loom [91]. Because of the stiff film formed by these polymers, they produce firm or stiff hands.

The thermoplastic resin latices such as butadiene-styrene, butadiene acrylonitrile, polyvinyl acetate, and acrylics are water insoluble, and durability is primarily a function of adhesion to the fibers. Such latices are more durable finishes for abrasion resistance than the water-soluble types and produce a variety of fabric hands ranging from very soft to very stiff depending upon the softness or hardness of the polymer, adhesion to the fibers, particle size, and amount of material added [114]. Butadiene-acrylonitrile or nitrile latex has been found to be durable to laundering and has been used as a finish for warp yarns during weaving and as an after-treatment for fabrics [154, 195]. Few actual wear tests have been reported to confirm the improved laboratory abrasion resistance measured on fabrics treated with these latices, but one test, involving 100 children, has shown that blue jeans made from nitrile latex-sized warp yarns provided from 50% to 75% more days of wear than jeans made from starch-sized yarns [50].

Lubricants. Instead of binding and restricting fiber motion, lubricants increase mobility by encasing fibers in smooth films. Textile lubricants are frequently of the fatty hydrocarbon type. Silicone and polyethylene compounds are also used [5, 115, 155]. Improvements in flex abrasion obtained with lubricants can be attributed to a reduction in surface friction and increased fiber movement resulting from reduced interfiber and interyarn friction. Studies show that too much lubrication can be harmful, however, because of increased fiber slippage [42, 54]. The effects of lubricants on flat abrasion have not been as clearly demonstrated, but the use of small amounts should provide some improvement as a result of reduction in surface friction.

Although laboratory abrasion resistance is improved, field tests conducted by the Army Quartermaster Corps have shown that the use of lubricants does not always improve wear life [13]. One field test indicated, for instance, that improvement was due in part to the reduced launderings resulting from the stain-resistant nature of the finish. Other tests incorporating uniform laundering practices showed little difference between treated and untreated materials over extended periods of use. This is not surprising, since the durability of most lubricants is limited.

Coatings. Coatings are an extreme case of additive finishing in that the fabric face is partially or completely covered with rubber, plastic, starch, or some other polymeric material [152].

Application of coatings to cotton is an old practice which began in this country as far back as 1800. The first coated fabrics were called "oil-cloth" since they were made by rubbing drying oils into the fabric, which was then hung in the sun to dry and harden. These early coated fabrics found application in uses such as protective clothing, tents, floor coverings, and table cloths. "Oil skins" used by commercial fishermen for generations were of this type.

Coatings provide protection to cotton fabrics from external abrasion, but where considerable flexing occurs, a coating is of less value. Such coatings as pyroxylin and oils are easily cracked or separated from the base fabric during repeated flexing. Depending upon the adhesive bond between the coating material and the fabric, even the more elastic films such as vinyl and rubber can separate on flexing, although cotton is known to provide the highest degree of adhesion. Finally, should the coating material be too deeply imbedded within the fabric structure, flex life of the fabric itself may be lowered because of reduced fiber and yarn mobility.

Coating techniques have been developed which provide increased abrasion resistance and at the same time permit transmission of water vapor. One technique consists of partially coating the fabric face so that protection from abrasion is achieved but water vapor can be transmitted through the uncoated areas. "Plastic-Dot" work gloves are an example of this application. The palms and fingers of the gloves are covered with small vinyl plastic dots of sufficient number to afford substantially improved abrasion resistance while leaving enough exposed fabric surface to reduce loss of comfort. Attractive

cotton fabrics for upholstery applications have also been developed employing the same principle.

Water impermeable, water vapor permeable cotton fabrics have also been obtained by imbedding coating materials inside the fabric, leaving fibers exposed on both surfaces to transmit water vapor but not liquid water [56].

Finishes—Chemical

Chemical finishes modify cotton cellulose by reacting inside or at the surface of the fiber. Such finishes have different effects on the abrasion resistance of cotton, depending on the nature of the finish. Some agents alter abrasion performance because they affect fiber mechanical properties. Others produce fiber swelling, which causes fabric shrinkage in addition to affecting the surface characteristics of the fiber.

Finishes for wrinkle resistance. As mentioned, finishes for wrinkle resistance markedly lower the abrasion resistance of cotton as measured by accelerated laboratory tests. The loss in abrasion performance is believed to result mainly from changes in fiber mechanical properties. The continually expanding market for resin-treated cottons indicates, however, that their mechanical properties have not been reduced below levels necessary to maintain adequate wear resistance under normal conditions of service use. In many instances, losses in abrasion and tensile properties resulting from resin treatment have been compensated for by the use of stronger fabric constructions. Where service conditions of abrasion are quite severe, however, more pronounced reductions in wear life of resin-treated cotton can be expected.

Mercerization. The abrasion resistance of mercerized cotton appears to be as good as or better than that of untreated cotton, as measured by various laboratory tests [38, 206]. Flat abrasion performance is little affected by either slack mercerization or mercerization under tension. The most significant improvements seem to be in the flex abrasion resistance of slack mercerized cotton. In mercerization under tension, such improvement in abrasion resistance as might be expected to result from increased fiber strength is probably offset by a reduction in yarn extensibility. In slack mercerization, improved abrasion performance can be attributed largely to the increased thread count that results from the fabric shrinkage caused by fiber swelling.

Cyanoethylation and acetylation. Acetylation and cyanoethylation increase flat abrasion resistance but have an adverse effect on flex abrasion resistance [28, 66]. Remarkable improvements in flat abrasion performance have been reported at high cyanoethyl substitution. The response of these chemically modified cottons to the two abrasion actions bears a striking resemblance to that of cotton treated with certain binding agents. Explanation of the peculiar abrasion performance of these chemically modified cottons is not simple, but several possibilities can be suggested.

Increased flat abrasion resistance may result from two effects. First, fiber swelling and the added weight of the substituted groups accompanying these modifications result in more densely packed fabrics, increasing the surface area exposed to abrasion. Second, high degrees of acetylation and cyanoethylation make cotton thermoplastic so that the fibers can yield more readily to abrasive force. The denser packing of the fibers, however, reduces flex abrasion resistance because of increased interfiber friction. Additional increases in interfiber friction may also result from removal of surface wax from the cotton fiber by the reaction media. Flex abrasion performance of partially acetylated cotton can be improved by the addition of proper lubricating agents [39].

Most other types of chemical modification, such as carboxymethylation and reaction with β-propriolactone, affect abrasion resistance of cotton [35]. Carboxymethylated cotton when prepared in an aqueous medium is the only chemically modified cotton which appears to have both improved flat and flex abrasion resistance is the result of a higher flex abrasion resistance. It is likely that improved retention of the lubricating surface wax on cotton fibers by the aqueous medium.

Abrasion Testing

Attempts to produce a uniform, constant, and reproducible abrading action which simulates and, if possible, correlates with service wear have resulted in the development of more abrasion testing devices than perhaps any other type of textile testing apparatus. Prior to 1946, more than 50 abrasion and wear testing machines had been developed [43]. Approximately 16 abrasion testers were developed before 1948 in Germany alone [148]. Within the past decade many others have been developed both in the United States and elsewhere.

Abrasion Tests and Prediction of Service Wear

Laboratory abrasion tests are valuable in both research and quality control, but authorities agree that presently available methods should not be relied upon to predict actual wear life of fabrics unless adequate service tests have proved the relationship between them.

When laboratory abrasion is compared with that encountered during actual wear, the danger involved in drawing far-reaching conclusions from laboratory tests alone becomes evident. First, an accelerated test requires that laboratory machines destroy specimens at rates far exceeding those that occur in service use [118, 150]. Also, the nature of the abrading action produced in the laboratory may not resemble that occurring in service. For example, the cutting action produced by most abrasive papers is rarely encountered in actual wear situations [150, 164]. Finally, abrasion is but one of a whole complex of variables involved and, under service conditions, the contribution of abrasion alone to the total wear process is not known. An understanding of the actual wear process can be obtained only by conducting service tests and salvage studies.

Such a salvage study was conducted by the Office of the Quartermaster General on cotton fabrics used for military fatigue uniforms [164, 196]. It was estimated that the mechanical factors in the wear of fatigue uniforms consisted of 30% flat abrasion, 20% edge and projection abrasion, 20% abrasion by flexing and bending, 20% tearing action, and 10% other mechanical actions. The above figures were only approximations, since it was found impossible to differentiate all the mechanical actions that occurred during wear. The study did indicate, however, that laboratory tests involving a combination of flexing, abrasion, and tearing should best correlate with this particular type wear, since these were shown to be the major wear actions. Laboratory indices based upon weighted values of flex abrasion, flat abrasion, and tear resistance have in fact shown excellent correlation with military combat course type wear [196].

The important point to be derived from the above example is that abrasion resistance as measured on one specific machine involving one specific type of abrading action is not sufficient for evaluation of wear resistance, especially in those end uses where other types of mechanical action contribute to breakdown. In the case just cited, for example, flat abrasion resistance alone showed comparatively little relationship to wear.

Another more recent example of reported correlation between laboratory and service tests has been the use of the "Duty Factor" for predicting wear occurring at the raised portions of resin-treated rayon staple fabrics such as collars, cuffs, pleat folds, and raised seams [24]. Values of flex abrasion and abrasion by the reciprocating action of a small steel ball were combined into an empirical mathematical expression termed the "Duty Factor" which was claimed to correlate quite well with this particular type of service wear. Flat abrasion tests, on the other hand, were found to be inadequate.

Conditions of Abrasion Testing

One essential principle governs the operation of abrasion testing devices developed to date. That is, the test specimen is rubbed, and in some machines also flexed, in such a manner that the amount of rubbing can be measured and the resultant damage to the specimen recorded. Abrasion resistance is determined by noting the amount of abrading action to produce a given amount of damage or by comparing the amount of damage produced for a given abrading action. In either case the higher the ratio of abrading action to amount of damage produced, the better the abrasion resistance. On any given machine the results obtained are sensitive to the following test conditions, variations of which can cause considerable nonreproducibility: general conditions of the test, such as wet or dry abrasion; nature of the abradant; nature of the motion between specimen and abradant; pressure and tension on the specimen; removal of debris produced during the test; and method of evaluation of the amount of abrasion damage.

Most abrasion testing is conducted in a standard atmosphere of 65% relative humidity and 70° F. unless other conditions are specified or it is known that the abrasion resistance of the specimen is unaffected by moisture content. During wet abrasion, specimens are immersed in water prior to testing or are continually wet during the test according to instructions which vary with the tester used.

It is most important that the action of the abradant remain constant during a given test and between successive tests for as long a period as possible [147, 164]. Otherwise, abradants must be changed frequently or a calibration be kept in order to apply

a correction to the results obtained. The abrasive power of most abradants decreases with use. Particularly is this true of abrasive papers such as emery or carborundum and fabric abrasives. Blade type abradants remain constant over fairly long periods of use, although anomalous results have been reported in tests with wool fabrics, where the rate of abrasion increased tenfold in a matter of a few minutes [149]. The unusually rapid increase in observed abrasive action was caused by the formation of a coating tenaciously held on the surface of the blade abradant. Careful examination showed the coating to consist of extremely small particles of wool, some of the order of 100–200 Å which appeared to correspond in shape and size to the elemental structural units previously proposed for the structure of wool.

It is likely that transfer of fiber material or finishing agents to the abradant frequently contributes to the discrepancies so often noted in abrasion test results. Abrasion testing authorities urge that anomalous results not be discarded but studied thoroughly to determine the cause, as in the instance cited above. Knowing the causes of such anomalies should help provide a better understanding of the complex mechanisms of abrasion.

Rubbing action is achieved in most machines by either a reciprocating or a circular motion between the abradant and the specimen. A counting device is attached to the tester so that the number of reciprocating strokes or rotations of the abradant over the specimen is recorded. It is important, however, that uniform abrasion take place over the area being tested. A mathematical study of the problem of producing uniform abrasion has been incorporated in the development of the Schiefer testing device [144]. In some instances unidirectional reciprocating action is desirable so that warp and filling directions of test fabrics can be evaluated separately. In addition, it is important that the pressure and tension on the specimen be recorded and kept constant throughout the test. The need to employ uniform pressure and the marked influence of specimen tension on test results have been discussed in considerable detail [164].

The accumulation of lint, pills, and other debris formed during abrasion tests can interfere with proper contact between specimen and abradant and cause inaccurate test results. The design of some testers minimizes the accumulation of such debris so that the test does not have to be interrupted. Others employ separate vacuum attachments. With nearly all testers, some provision for removal of debris is necessary if accurate and reproducible results are to be obtained.

Determination of the end-point is a most important aspect of abrasion testing. A measure of the abrasion resistance of the test specimen depends upon an accurate method of evaluating the amount of damage which took place. In many tests the specimen is abraded to destruction, as evidenced by hole formation or rupture, and the number of cycles or rotations is recorded. Some machines automatically stop when the specimen is destroyed. However, the effects of abrasion on a specific property of the specimen or the rate at which it is destroyed cannot be evaluated because the test is run without interruption.

Other methods of evaluating abrasion damage involve noting the effect of abrasion on changes in such properties as weight, thickness, breaking strength, electrical capacitance, air permeability, etc., which can be more or less dependably measured on a quantitative basis. The selection of the property to be evaluated depends upon the specimen being tested and the importance of the property in a particular end-use application. For most woven fabrics and yarns, measurement of changes in thickness is not a reliable criterion because of the small differences involved. Loss in breaking strength, however, is a convenient method of measurement. In

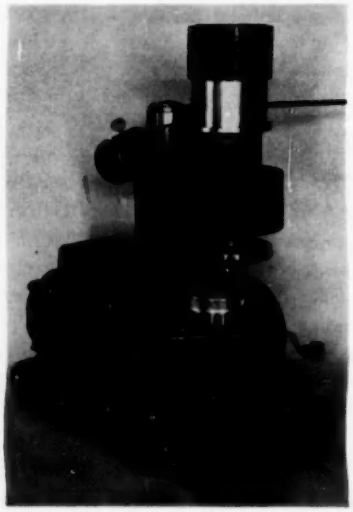

Fig. 16. Schiefer Abrasion Machine.

such items as carpets, pile fabrics, or heavy woven goods, weight loss or thickness measurements can be more practically utilized. The NBS carpet tester employs a special thickness measurement technique for evaluating the abrasion resistance of carpets [145]. Elaborate methods of evaluating abrasion damage by measurement of electrical capacitance and air permeability have also been reported [147].

Visual methods of evaluation may be employed, such as noting the effects of abrasion on color, luster, pilling, or other surface characteristics of the specimen. Such methods are subject to error because they depend on judgment of the operator, but they can be useful should appearance be the primary factor determining serviceability.

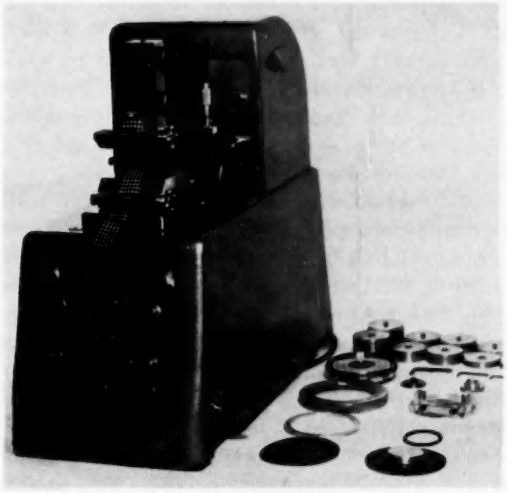

Fig. 17. Stoll tester.

Fig. 18. Taber Abraser.

Commonly Used Testers

A brief description of the testers more commonly used in this country is given below.

Schiefer machine. Development of this machine was based upon a mathematical approach to the problem of producing uniform abrasion [8, 144, 147]. Figure 16 depicts a commercially available model. Abrasion action is produced by rotation of both the abradant and the specimen in the same direction but at slightly different angular velocities. The axes of rotation of the specimen and the abradant are separate but parallel, and the abradant surface is sufficiently larger than that of the specimen so that the entire surface of the specimen is in contact with some portion of the abradant at all times. The result is that with each rotation of the two surfaces, every point on the specimen is abraded equally in all directions and comes into contact with a different portion of the abradant. The machine is adaptable to a wide range of testing conditions and textile articles.

Stoll tester. The rubbing action in the Stoll tester is a reciprocating motion between the abradant and the specimen [8, 164]. Figure 17 shows the Stoll tester and a fabric specimen ready for a flex abrasion test. The fabric, fastened to a reciprocating table, passes over a steel bar or blade abradant which maintains it in a folded condition during the test. For flat abrasion tests, the specimen is placed in a circular clamp over a rubber diaphragm under which controlled air pressure is maintained. The clamp assembly is attached to the reciprocating table so that the specimen is rubbed back and forth against the stationary abradant located under the upper plate in Figure 17. Flattening of the inflated diaphragm by the load on the abradant assures uniform pressure between the specimen and the abradant. Provision is made for rotation of the clamp, in addition to the reciprocating motion, so that multidirectional abrasion can be obtained.

Taber abraser. A commercially available model of this machine is shown in Figure 18 [8]. Specimens approximately 5 in. in diameter are mounted in a circular platform which rotates horizontally.

Mounted above the platform are two abrasive wheels which are free to rotate vertically as a result of the rotation and frictional action of the platform. The abrasive wheels are ½ in. thick and thus produce a circular abraded path of the same dimension on the specimen. Rubber-base or vitrified-base type wheels of various abrasive qualities are used.

Wyzenbeek abrader. Figure 19 shows this tester, in which unidirectional rubbing action is achieved by an oscillating cylinder over which is mounted a sheet of abrasive material, usually emery paper [8]. As shown in the figure, specimens are mounted in holding arms and rest against the curved surface of the cylinder, which oscillates through a 3-in. arc at the rate of 90 cycles/min.

Accelerotor. The Accelerotor is illustrated in Figure 20 [38]. A fabric specimen is driven by an impeller (rotor) in a random path so that it repeatedly impinges on the walls and abradant liner within the chamber shown in Figure 20. The specimen follows a zigzag course in a generally circular orbit and is subjected to abrasion, flexing, shock, compression, and stretching. An automatic timer allows rotation of the impeller at constant revolutions per minute for a predetermined period of time.

Other testers are those described by Sulser [173], the LINRA tester [6], the BFT Mark III machine [24], and the Stout machine [171]. A U. S. patent also describes a yarn testing apparatus designed to imitate abrasion of warp yarns in the heddles and reed of the loom during weaving [91].

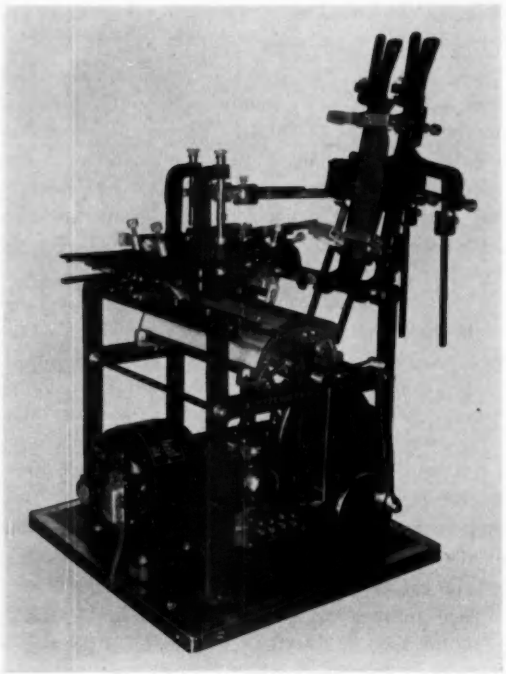

Fig. 19. Wyzenbeek Abrader.

Service Tests

Accelerated laboratory tests have only limited value in predicting the relative performance of fabrics during actual service [150]. For the present, therefore, only service tests can provide truly reliable information on abrasion resistance. Few such tests have been conducted because of the complications, cost, and time involved. However, accelerated wear trials represent one method of obtaining more realistic evaluations of abrasion performance without the time and expense involved in longer duration service tests [83, 196]. Accelerated wear tests conducted on the Combat Course of the Quartermaster Corps have been of great value in determining optimum fabric construction for abrasion resistance of military fatigue uniforms.

Such wear trials are also useful for evaluating abrasion performance of textiles in civilian applications. For example, carpets can be evaluated for abrasive wear by accelerated service tests. Recent carpet wear tests conducted in New York's busy Pennsylvania Station are a good illustration [159]. An advantage of accelerated wear tests over large scale consumer tests is the greater control that more regimented procedures provide [196].

Research Topics

Much study has been given to the effects of construction and to the development of testing devices, but much work remains to be done in studying the mechanism of abrasion and correlating laboratory tests with actual wear life. The following sugges-

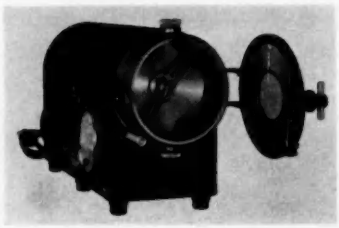

Fig. 20. Accelerotor.

tions are presented in hope of stimulating research and thought in those areas that have received little attention but appear to hold some promise.

Mechanism of Abrasion

Much remains to be learned about the basic mechanisms of abrasion. Although abrasion damage to cotton textiles proceeds through the gross mechanisms of direct fiber damage and the untwisting, displacement, or removal of fibers in the yarn, the detailed processes involved are extremely complex and not well understood. Microscopic observation of cotton fibers and yarn structures damaged under controlled abrasion could help to determine the relative importance of the two mechanisms. Observation of changes in yarn structure throughout the course of abrasion might yield particularly useful information. The electron microscope could be especially helpful in studying the surfaces of abraded cotton fibers.

Observation of damaged fibers taken from externally abraded yarns and fabrics might also help to establish the relative importance of fiber mechanical properties. The damage observed could be compared to that typical of tensile, shear, or flexural failure of single cotton fibers. Examination of cotton fibers taken from fabrics subjected to flexing without external abrasion would likewise help to determine the relative contribution of failure due to fiber bending versus that resulting from interfiber friction. Wet and dry abrasion should be compared. It might be expected that in the wet state abrasion damage proceeds more through fiber slippage than in the dry.

In certain applications, such as accelerated laboratory testing, frictional heat developed during abrasion may be an important factor. Studies with steel surfaces have shown that heat effects can alter the surface properties of metals through the media of phase changes and chemical combination with atmospheric elements or contaminants [33, 197]. Such surface effects were associated with changes in the wear pattern of the steel surfaces. It has been demonstrated that fundamental changes in physical and chemical structure occur when cotton fibers are exposed to heat in the presence of air and moisture [182]. Demonstration that such changes occur during abrasion of cotton would yield a clearer picture of the mechanism of laboratory abrasion.

Fiber Mechanical Properties

Shear properties of fibers have received less attention than tensile. Further evaluation of the inherent abrasion resistance of fibers using different abrasive surfaces is needed to establish the relative importance of tensile and shear properties [174]. When sharp abrasives are used or conditions in the yarns do not permit free mobility and yielding of fibers, abrasion resistance should be more dependent upon shear properties. Since shear and tensile properties of cotton depend on its fibrillar orientation, it may be possible to show a relationship between abrasion performance and fibrillar orientation as determined by x-ray angle measurements [131].

A study of the abrasion performance of resin-treated cotton under variously accelerated laboratory test conditions should have merit. The importance of increased elastic recovery of cross-linked fibers should become evident at lower rates of abrasion, where fibers have more time to recover from abrasive forces. If the differences in abrasion resistance between resin-treated and untreated cotton should be nearly the same at all rates of testing, it would indicate that reduced extensibility and strength resulting from resin treatment outweigh increased elastic recovery.

Yarn and Fabric Structure

The effects of yarn and fabric structure on flex abrasion have been given much less attention than their effects on flat abrasion. Dense or tight structures enhance surface abrasion resistance but have an adverse effect on flex abrasion [29]. Poor resistance to one abrasive action cannot be compensated for by good resistance to another. Where mechanical failure in service results mainly from surface abrasion, the use of dense or tight structures should prolong wear life. On the other hand, when considerable flexing occurs, employment of the same construction may result in early failure. Future work on fabric construction should therefore include the determination of designs which provide optimum resistance to both surface and flexing abrasion.

A comparison of the wet and dry abrasion performance of cotton as a function of fabric construction would be a worthwhile extension of the little information so far reported. Marked differences should be interpreted in the light of increased strength, fiber swelling, and fiber slippage resulting from the presence of water. Thus, the stiffening

effect of fiber swelling might not be harmful with loose constructions but could act to lower flex abrasion performance with dense constructions.

Fiber Modification

Cotton fibers with enhanced abrasion resistance properties should be obtainable through breeding and through chemical modification.

Breeding practices which produce longer fibers are beneficial. Improved fiber cohesion and stronger yarns and fabrics can be expected with increased staple length. Length should not be achieved at the expense of greatly increased fineness, however, because the improvements in cohesion would be offset to some extent by the easier rupture of very thin fibers. Attempts to grow longer fibers solely for the purpose of increasing abrasion performance may not be justified. However, since such qualities as tensile strength, crease resistance, and luster would also benefit to one degree or another by increased staple length, continued efforts to breed longer fibers have sufficient justification.

Improvements in the elastic extensibility of cotton fibers through chemical and physical modifications should result in increased abrasion performance of yarns and fabrics. At the same time, however, the excellent transverse properties (shear) of cotton should not be sacrificed. In addition to abrasion resistance, wrinkle recovery and warmth retention properties of cotton would also be enhanced by improvements in elastic extensibility.

The effects of chemical modifications should be further studied and any marked changes in abrasion resistance should be related to new fiber, yarn, or fabric properties resulting from the modification. Cyanoethylation and acetylation, for example, increase the cross-sectional area and reduce the gross surface irregularities of cotton fibers [186]. How such changes are related to the abrasion performance of cyanoethylated and acetylated cotton remains to be determined. Although such chemical modifications themselves may not be an economical approach to increased abrasion resistance of cotton, an understanding of the mechanisms through which these modifications enhance abrasion resistance may suggest economically more feasible methods.

Additive Finishes

A need exists for finishes which provide durable abrasion resistance and do not impair appreciably the hand, appearance, or other desirable properties of cotton textiles. Nitrile latex applications represent advancement along these lines. Binding agents which physically protect the fiber should not at the same time cause excessive restriction of fiber movement needed to prevent damage from flexing. Latices or other binding media which have excellent adhesion qualities and yet are sufficiently extensible and elastic in themselves would be ideal in that fiber binding could be achieved with less loss in fiber movement.

Applications such as upholstery, footwear, and special industrial protective clothing require high levels of abrasion performance and water resistance, plus sufficient vapor permeability to prevent objectionable loss of comfort. Conventional coated cotton fabrics are deficient in vapor permeability because the coating material completely covers the fabric.

By using relatively fluid coating mixtures and by scraping hard to remove excess material, coatings can be imbedded inside cotton fabrics, leaving the fibers exposed on both surfaces to transmit water vapor [56]. Water impermeable, water vapor permeable cotton fabrics have been developed using this technique and have found commercial applications in such items as work gloves. Scraping the fabric surface to remove excess coating produces an unattractive appearance and feel, however, and limits the use of these fabrics to applications where appearance or hand are not important considerations. Methods of depositing coating materials inside cotton fabrics so that abrasion resistance is improved while hand and appearance are not adversely affected should improve the market potential for wear and water resistant, water vapor permeable cotton fabrics.

Testing Methods

There is a serious need for a method to relate accelerated abrasion testing with actual wear life. Considering the numerous factors affecting wear life and the marked differences between laboratory and service abrasion conditions, it is not surprising that laboratory abrasion tests have not succeeded in adequately predicting service performance of textiles [150].

An understanding of the major causes of failure in service is first needed. Attempts should be made to distinguish chemical from mechanical effects in

the over-all wear process. The contribution of various mechanical factors to failure should then be determined. Salvage studies of service-worn textiles can help to determine the degree of damage caused by direct rubbing, external tensile stress, flex abrasion, tearing, and other factors.

Laboratory tests should then be based upon the chemical and mechanical factors known to be major contributors to failure in service. With very dense constructions, for example, laboratory tests for flat abrasion resistance and tensile strength would indicate wear life superior to that of more open structures. Should considerable flexing occur in service, however, the laboratory results would be misleading because flex abrasion resistance of very dense constructions is considerably lower than that of more open structures. Binding agents are known to improve flat abrasion resistance, and lubricants increase flex abrasion resistance. It should be obvious that improvement in laboratory abrasion performance resulting from addition of binding agents and lubricants has little significance if such materials are readily removed in laundering or other conditions in service.

In end uses where abrasion is known to be the controlling factor in wear life, the relationship between laboratory abrasion tests and performance should be less complex. Accurate interpretation of laboratory test results remains a problem, however, as long as the rate and type of laboratory abrasion are so markedly different from that of service.

Aside from the important factor of correlation with service wear, much work also remains to be done to improve the reproducibility of abrasion testing machines. Despite the concerted effort that has gone into the development of numerous testers over the years, the need for a reliable tester still exists. Laboratories concerned with abrasion testing on a day-to-day basis are dissatisfied with the reproducibility of currently available testers. Development of new machines and improvement of existing ones to achieve reproducibility and correlation between laboratories, machines, and operators is an important objective.

Some authorities feel that an engineering approach [69] to the design and use of textiles can eventually be used to replace laboratory abrasion tests [41]. Such an approach would consider the stress–strain properties of individual fibers as well as fabric construction. Filament structures should be more subject to engineering analysis than staple fiber fabrics, because the mechanics of staple yarns are more complex than those of filament yarns. For natural fibers such as cotton, additional complications will result from the inherent variability of stress–strain properties of individual fibers. Finally, the effects of variations in processing conditions and chemical finishing on fiber properties will have to be reconciled.

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It should not be inferred that the technical opinions expressed in this report are necessarily those of the authorities listed above.

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Stress-Strain Relationships in Yarns Subjected to Rapid Impact Loading

Part VI: Velocities of Strain Waves Resulting from Impact

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Abstract

When a textile yarn is impacted transversely, strain waves and transverse waves which travel outwards away from the point of impact are initiated. Each strain-wave front travels at constant velocity. A transverse-wave front, however, changes its velocity each time it meets a reflected strain-wave front. This effect forms the basis of a new method used to measure strain-wave propagation velocities in a selection of textile yarns. Velocities obtained in this way are in good agreement with velocities obtained by two other methods. These velocities range in values from 1400 m./sec. for undrawn nylon to 5000 m./sec. for high tenacity rayon and glass fiber.

WHEN a yarn is struck transversely by a projectile, two longitudinal strain waves are initiated which propagate in opposite directions away from the point of impact. In the region between the two wave fronts, material of the yarn is set into motion towards the point of impact. This inward-flowing material forms itself into a transverse wave shaped like an inverted "V" with the impacting projectile at the vertex. The front of the transverse wave travels along the yarn at a constant velocity that depends on the magnitude of the preceding strain wave. If the yarn is clamped at a suitable distance from the point of impact, the strain wave will be reflected, and on its return journey will interact with the transverse-wave front, causing it to increase in velocity. From a photographic record of yarn configurations at various times after impact, it is possible to determine the time required for the longitudinal-strain-wave front to travel from impact point to clamp and back to the transverse-wave front. Thus the velocity at which the strain-wave front travels can be calculated.

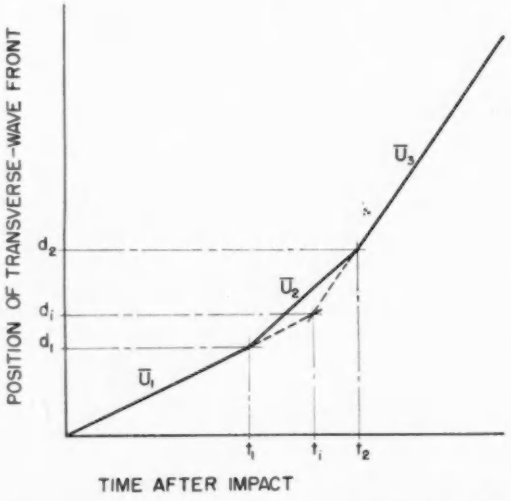

Fig. 1. Position of transverse-wave front as a function of time after impact, for a long clamped textile yarn impacted transversely.

Strain propagation velocities directly obtained in this way constitute data of considerable value in the analysis of impact problems. Consequently, the method just outlined has been used to measure these velocities for a number of textile yarns. The results obtained have then been checked by comparing them with results obtained by two other methods.

Preliminary Estimate of the Strain-Wave Velocity

Consider a yarn held between two clamps a distance $2L$ apart. Let this yarn be impacted transversely at the midpoint by a projectile flying at velocity V. The position of the resulting transverse-wave front moving along either half of the

yarn is shown in the position–time plot of Figure 1. In this plot, impact occurs at time zero. The transverse-wave front moves along the yarn at velocity $\bar{U}_1$ until time t_1, when it meets the returning strain wave and speeds up to velocity $\bar{U}_2$. The transverse wave proceeds at velocity $\bar{U}_2$ until time t_2. At this time the strain wave, after reflection at the projectile, overtakes the transverse wave and again causes it to speed up, this time to velocity $\bar{U}_3$. The transverse wave then continues along the yarn at velocity $\bar{U}_3$.

If the small change in yarn length due to strain is neglected, the velocity C of the strain wave, as calculated from the data of Figure 1, is equal to $(2L - d_1)/t_1$, where d_1 is the position of the transverse-wave front (with respect to the laboratory) at time t_1. In practice, however, it is often difficult to locate the point (t_1, d_1) accurately, because the transverse-wave front travels at velocity $\bar{U}_2$ for only a short time. Thus there are not enough data to determine precisely the position or slope of the segment between points (t_1, d_1) and (t_2, d_2). The point (t_i, d_i) where the lines corresponding to velocities $\bar{U}_1$ and $\bar{U}_3$ intersect can, however, be used to obtain a first approximation to the strain-wave velocity by the following method.

During the time interval from t_1 to t_2, the strain-wave front travels from the transverse-wave front to the projectile and back again to the transverse-wave front. The time at which the strain-wave front arrives at the projectile corresponds closely to the time t_i. Thus during the interval until time t_i the strain wave front travels approximately a distance $2L$, or twice the unstrained specimen length from impact point to clamp. The value $C = 2L/t_i$ is therefore a good first approximation to the strain-wave propagation velocity.

By using this approximate value of C it is possible to estimate the position of the point (t_1, d_1) and thereby obtain a more accurate value. The refinements necessary for this calculation, however, require knowledge of a transverse-impact theory that has been developed in a previous publication [6]. The essential results of this theory, simplified by the assumption that the textile yarn has a linear tension–strain curve,[1] are reviewed in the next section.

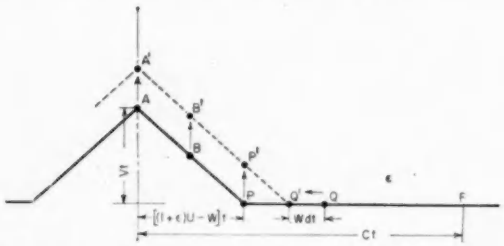

Fig. 2. Configuration of a textile yarn t sec. after transverse impact. The yarn, originally horizontal, was impacted at velocity V in the vertical direction. After t sec., the resulting strain wave propagating in the positive direction has its wave front at F. The yarn in the region traversed by the wave is strained by an amount ϵ. The more slowly propagating transverse wave has the configuration ABPQ. After $t + dt$ second the configuration becomes A'B'P'Q'. Yarn material in the transverse wave moves vertically with velocity V. Material in advance of the transverse wave moves inward horizontally with velocity W. The transverse-wave front moves with velocity U relative to points on the unstrained yarn, but the horizontal component of its velocity, or velocity $\bar{U}$ with respect to the laboratory, is $(1 + \epsilon)U - W$. The point Q on the yarn moves inward to position Q', the location of the transverse wave front at time $t + dt$.

This description has been simplified by assuming that the yarn has a linear stress–strain curve. This assumption is valid if the impact velocity V is sufficiently small.

Theory of Transverse Impact

The configuration of the yarn at a time t after impact is shown in Figure 2. To understand what happens in this yarn, consider the sequence of events as they would appear to a particle of yarn at a distance x from the point of impact as measured along the unstrained yarn. Let the yarn lie horizontally and be impacted at velocity V in the vertical direction. After impact, the particles does not experience any effects until the strain-wave front reaches it at a time x/C later. At this time the strain suddenly increases to the value ϵ and the particle starts to move inward with velocity W towards the point of impact. The strain-wave velocity C relative to points on the unstrained yarn is given by

$$C = \sqrt{\frac{1}{M}\left(\frac{dT}{d\epsilon}\right)_{\epsilon=0}} \qquad (1)$$

where M is the mass of unit length of unstrained yarn, and $(dT/d\epsilon)_{\epsilon=0}$ is the initial slope of the tension–strain curve. The velocity W of material flow is given by

$$W = C\epsilon \qquad (2)$$

[1] The tension–strain curves of most textile yarns are linear for the small strains encountered in the experiments described here. Because of this linearity the strain wave has a single steep sharp front, and the strain jumps from zero to the final value as the wave front passes.

After the strain wave has passed, the strain and the velocity of horizontal flow of the particle remain constant until time x/U. This is the time of arrival of the transverse-wave front. At this instant the particle stops moving horizontally and moves abruptly in the vertical direction at impact velocity V. The strain ϵ at the particle remains constant. The velocity U of the transverse wave relative to points on the unstrained yarn[2] is given by

$$U = \sqrt{\frac{T}{M(1+\epsilon)}} \tag{3}$$

where T is the tension in the yarn.

Equations 1, 2, and 3 give the velocities C, W, and U as functions of the known quantities T, M, and $(dT/d\epsilon)_{\epsilon=0}$ and the unknown quantity ϵ. One other relation is needed to find ϵ in terms of the known variable V and the other known quantities. This final relation is

$$V = \sqrt{(1+\epsilon)^2U^2 - [(1+\epsilon)U - W]^2} \tag{4}$$

Now consider the behavior of the yarn from the standpoint of an observer in the laboratory. At time t after impact the outermost portions of the yarn are horizontal and motionless. At a distance Ct from the point of impact, the yarn material becomes strained and moves inward toward the point of impact. In this region between the strain-wave front at Ct and the transverse-wave front at $\bar{U}t$ the yarn has strain ϵ and moves at velocity W. The transverse-wave front travels with velocity U relatively to the unstrained yarn, but because of the strain and movement of the yarn, the velocity of the transverse wave front with respect to the laboratory is $\bar{U}$, given by

$$\bar{U} = (1+\epsilon)U - W \tag{5}$$

The above analysis assumes Hookean behavior, so

$$T = MC^2\epsilon \tag{6}$$

Equations 3, 4, and 5 thus reduce to

$$U = C\sqrt{\frac{\epsilon}{1+\epsilon}} \tag{7}$$

$$V = C\sqrt{\epsilon(1+\epsilon) - [\sqrt{\epsilon(1+\epsilon)} - \epsilon]^2} \tag{8}$$

$$\bar{U} = C[\sqrt{\epsilon(1+\epsilon)} - \epsilon] \tag{9}$$

[2] The velocity U is expressed relative to a Lagrangian coordinate system; i.e., a system fixed to the yarn, moving and extending with it.

Calculation of the Strain-Wave Velocity

Suppose, according to Figure 1, that the strain-wave front, after reflection at the clamp, meets the transverse-wave front at time t_1. The distance with respect to the laboratory that the strain-wave front travels during this time is L plus the strained segment $(L - d_1)$. Since the strain in this segment is 2ϵ, the corresponding length of the segment before straining is $(L - d_1)/(1 + 2\epsilon)$. Therefore, with respect to the unstrained yarn, the strain-wave front travels a distance of $L + (L - d_1)/(1 + 2\epsilon)$; that is, $(2L + 2\epsilon L - d_1)/(1 + 2\epsilon)$. Thus the strain-wave velocity in the unstrained yarn is given by

$$C = \frac{2L(1+\epsilon) - d_1}{t_1(1+2\epsilon)} \tag{10}$$

The strain wave continues on towards the impacting projectile, is reflected, and on its return overtakes the transverse wave at time t_2. The distance the wave travels with respect to the unstrained yarn is

$$3L - \frac{L - d_2}{1+2\epsilon} = \frac{2L(1+3\epsilon) + d_2}{1+2\epsilon}$$

Thus the strain-wave velocity can also be obtained from the formula

$$C = \frac{2L(1+3\epsilon) + d_2}{t_2(1+2\epsilon)} \tag{11}$$

The magnitude of the strain ϵ can be estimated by use of Equation 8. For convenience, values of V/C are first calculated for various values of ϵ and the results plotted as a curve. The strain ϵ in the yarn can then be determined from the impact velocity V and the approximate value for the strain-wave velocity $C = 2L/t_1$. This value of ϵ, although approximate, is adequate for the cases treated in this paper.

In order to use Equations 10 and 11, the points (t_1, d_1) and (t_2, d_2) must be accurately determinable from the experimental data. As already mentioned, this is often difficult because the available data for the time interval t_1 to t_2 is insufficient. In such cases it is possible to calculate an upper and a lower limit for the velocity C, between which the true value of C must be contained.

Suppose, in Figure 1, that the points (t_1, d_1) and (t_2, d_2) cannot be precisely determined. In this case assume a likely position for the point (t_1, d_1), and from this assumption compute a value for C using Equation 10. Next assume a position for the

point (t_2, d_2) and compute a value for C using Equation 11. If the two values for C do not agree, a new location for the point (t_2, d_2) should be chosen by trial and error until agreement is obtained. The velocity $\bar{U}_2$ at which the transverse-wave front advances during the time interval t_1 to t_2 can then be found from the formula

$$\bar{U}_2 = \frac{d_2 - d_1}{t_2 - t_1} \tag{12}$$

Thus it is seen that for each position–time coordinate (t_1, d_1) of the transverse-wave front, chosen as a possible point of interaction with the strain-wave front, there corresponds a value of the velocity C, a value of the velocity $\bar{U}_2$, and a position–time coordinate (t_2, d_2) which are mutually consistent with the experimental results. Any number of such mutually-consistent values can be computed by assuming different positions for the point (t_1, d_1).

Suppose that the point (t_2, d_2) so found coincides with the the point (t_i, d_i). The corresponding point (t_1, d_1) then gives the earliest time at which the head-on interaction can occur. The corresponding value of C in this case is the maximum value that can be inferred from the experimental data, and the corresponding value of $\bar{U}_2$ is equal to $\bar{U}_1$. If, on the other hand, the point (t_1, d_1) is chosen to coincide with the point (t_i, d_i), the corresponding point (t_2, d_2) gives the latest time at which the overtaking interaction can occur. The corresponding value of C is then the minimum value that can be inferred from the experimental data, and the corresponding value of $\bar{U}_2$ is equal to $\bar{U}_3$. The true value of C is bounded by these two extreme values of C, just as the true value of $\bar{U}_2$ is bounded by $\bar{U}_1$ and $\bar{U}_3$.

The true value of the strain-wave velocity C can be even more closely bounded by narrowing the limits on the true value of $\bar{U}_2$. This is done by finding a value for the ratio $\bar{U}_2/\bar{U}_1$ that can never be exceeded and a value for the ratio $\bar{U}_2/\bar{U}_3$ that must always be exceeded. The values of these ratios have been accurately computed using theories developed by Craggs [2] and McCrackin (5), but the calculations are involved and not included in this paper. The essential ideas, however, are given in the following approximate analysis.

Consider the case in which the reflected strain-wave front meets the advancing transverse-wave front head-on. At this meeting an interaction occurs in which part of the strain wave is re-reflected towards the clamp, the remainder passing on towards the vertex of the transverse wave. For interactions of the magnitude dealt with in this paper, the portion of the strain that is re-reflected is small, and to a very good approximation the strain at the transverse-wave front is doubled. A similar interaction occurs when the strain-wave front, after reflection at the vertex of the transverse wave, overtakes the transverse-wave front. The strain at the transverse-wave front is then increased to almost three times its original value.

If ϵ_1 is the original strain at the transverse-wave front before any interaction occurs, the original transverse-wave front velocity $\bar{U}_1$ as given by Equation 9 is

$$\bar{U}_1 = C[\sqrt{\epsilon_1(1 + \epsilon_1)} - \epsilon_1] \tag{13}$$

After interaction with the reflected strain wave, the transverse-wave front travels along a strained but motionless medium at velocity $\bar{U}_2$ given by

$$\bar{U}_2 = C\sqrt{2\epsilon_1(1 + 2\epsilon_1)} \tag{14}$$

To obtain this formula the value of U given in Equation 7 is multiplied by the factor $(1 + 2\epsilon_1)$ to correct for the strain in the yarn and the strain ϵ is replaced by the strain $2\epsilon_1$. After interaction with the overtaking strain wave, the transverse-wave front propagates in a strained and moving medium at velocity

$$\bar{U}_3 = C[\sqrt{3\epsilon_1(1 + 3\epsilon_1)} - \epsilon_1] \tag{15}$$

The ratios $\bar{U}_2/\bar{U}_1$ and $\bar{U}_2/\bar{U}_3$ can be calculated from the Equations 13, 14, and 15, or from the expansions

$$\bar{U}_2/\bar{U}_1 = 2^{\frac{1}{2}}\left[1 + \epsilon_1^{\frac{1}{2}} + \frac{3}{2}\epsilon_1^{\frac{3}{2}} - \frac{1}{8}\epsilon_1^2 + \cdots\right] \tag{16}$$

$$\bar{U}_2/\bar{U}_3 = \left(\frac{2}{3}\right)^{\frac{1}{2}}\left[1 + \frac{\sqrt{3}}{3}\epsilon_1^{\frac{1}{2}} - \frac{1}{6}\epsilon_1 - \frac{5}{9}\sqrt{3}\,\epsilon_1^{\frac{3}{2}} + \frac{23}{72}\epsilon_1^2 + \cdots\right] \tag{17}$$

It is found from these formulas that, as ϵ_1 increases from 0.001 to 0.01, $\bar{U}_2/\bar{U}_1$ ranges in value from 1.46 to 1.58, and $\bar{U}_2/\bar{U}_3$ from 0.83 to 0.86. The more exact analysis in which the interactions are accurately calculated gives almost the same results. According to this analysis, as ϵ_1 increases from 0.001 to 0.01, $\bar{U}_2/\bar{U}_1$ ranges in value from 1.40 to 1.50, and $\bar{U}_2/\bar{U}_3$ from 0.86 to 0.88.

The strain pulse ϵ_1 resulting from the transverse

impact does not exceed 0.01 in any of the examples to be reported here. It follows that $\bar{U}_2$ can not exceed 1.50 $\bar{U}_1$. In the experimental work, the specimens are held in the "just taut" state before they are impacted and therefore have a small initial strain which may be comparable in magnitude with ϵ_1. As a consequence the velocity $\bar{U}_1$ is higher than that predicted by Equation 13. At the first interaction the strain changes from ϵ_1 plus initial strain to $2\epsilon_1$ plus initial strain. The resulting velocity $\bar{U}_2$ will be higher than that predicted by Equation 14, but the ratio $\bar{U}_2/\bar{U}_1$ will be lower than that given by Equation 16 or by the exact analysis. Thus one limit to the value of $\bar{U}_2$ is given by

$$\bar{U}_2 \leq 1.50\ \bar{U}_1 \tag{18}$$

A similar argument leads to the conclusion that

$$\bar{U}_2 \geq 0.88\ \bar{U}_3 \tag{19}$$

Since the effect of initial strain is less pronounced in the relationship between $\bar{U}_2$ and $\bar{U}_3$, the true value of $\bar{U}_2$ can be expected to lie closer to 0.88 $\bar{U}_3$ than to 1.50 $\bar{U}_1$. Similarly, the true value of C lies closer to the value of C corresponding to a $\bar{U}_2$ of 0.88 $\bar{U}_3$. The values of C reported in the work are taken equal to C_1 (corresponding to $\bar{U}_2$ = 1.50 $\bar{U}_1$) plus two-thirds of the interval between C_1 and C_2 (corresponding to $\bar{U}_2$ = 0.88 $\bar{U}_3$).

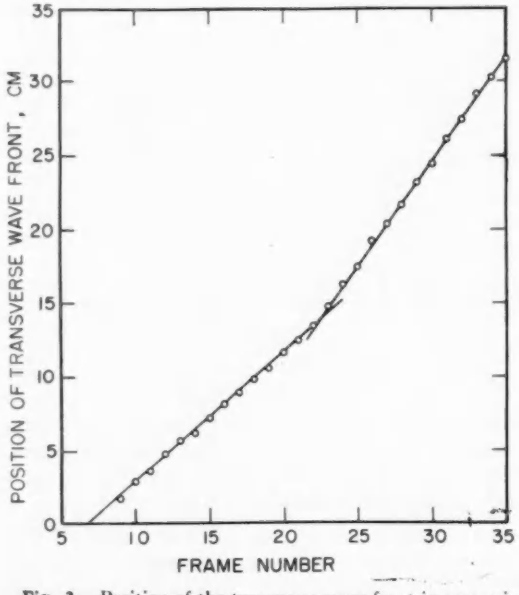

Fig. 3. Position of the transverse-wave front in successive frames of the photographic record, for example discussed in the text.

Application of the Method

The method just described was tested on a number of textile yarns, using a transverse-impact apparatus described previously [7]. As an example, a specimen of polyester yarn 310 cm. in length was clamped at each end and impacted at the midpoint by a flying projectile. Subsequent configurations of one-half of the yarn specimen were photographed with a high-speed camera at 15,444 frames/sec. Positions of the projectile and transverse-wave front with respect to a reference grid were measured in each frame of the photographic record obtained and the measurements plotted against frame number. A projectile velocity of 40 m./sec. was determined from one of these plots. The plot of transverse-wave front versus frame number is shown in Figure 3. Here it is seen that impact occurs at frame 6.70 and that the two lines with slopes corresponding to the initial velocity $\bar{U}_1$ and the final velocity $\bar{U}_3$ intersect at frame 22.3 and distance d_i of 13.69 cm.

The data and subsequent calculations for this example are given in Table I. Similar calculations were made for all of the yarns tested. The results obtained are discussed later in the text.

Other Methods for Determining Strain-Wave Velocity

By use of Equations 8 and 9 it is possible to express the quotient $V/\bar{U}$ as a function of ϵ alone. The strain ϵ resulting from a transverse impact could thus be obtained from experimentally-determined values of V and $\bar{U}_1$. The strain-wave velocity C could then be determined from Equation 9. It would not be necessary to determine the coordinates for the interaction of the transverse and strain-wave fronts. Unfortunately, although this method is simple in concept, the results obtained in most cases are uncertain because of the small tensile force applied in mounting the specimen. This force causes the experimentally determined value of $\bar{U}_1$ to exceed the theoretical value slightly. This slight indeterminacy in $\bar{U}_1$ causes a much larger error in the value of ϵ and a correpsondingly larger error in the value of C obtained. These errors could be decreased somewhat by measuring the static tension in the specimen and taking proper

account of it in the analysis, but this was not done in the experimental work reported here. Therefore, no values of strain-propagation velocity based on this method are reported.

The velocity C can be estimated from Equation 1 using for $(dT/d\epsilon)_{\epsilon=0}$ the initial slope of the tension–strain curve obtained with a conventional tensile testing apparatus. A value of C estimated in this way is usually less than the velocity at which the strain wave actually propagates. This may be inferred from the fact that the initial slope of a tension–strain curve is steepest when the test is performed at a very rapid rate.

A sonic-modulus technique frequently used for measuring C has been described by Ballou and Smith [1]. In this method a textile yarn approximately 2 m. long is strung along an optical bench. The yarn is fastened at one end to the stylus of a phonograph record cutter. The other end is passed over a small pulley and attached to a small tensioning weight. The record cutter is used to excite a train of longitudinal strain waves along the yarn. The sinusoidal voltage that drives the cutter is also impressed across the horizontal plates of a cathode-ray oscilloscope. The strain waves are detected by a rochelle salt crystal which is held in contact with the yarn and can be moved along the optical bench. The voltage output from this detecting crystal is impressed across the vertical plates of the cathode-ray oscilloscope. The difference in phase between the driving voltage and the pickup voltage can be detected by observing the Lissajous figure formed on the face of the oscilloscope.

Measurements with this apparatus are quite simple. The pick-up crystal is moved along the textile yarn and points are found at which the Lissajous pattern indicates that the phase has changed by 180°. The distance between these points equals one-half wave length of the sinusoidal strain wave propagating along the yarn. Since the frequency ν of this oscillating strain wave is

TABLE I. Data and Calculations for Example Discussed in Text

Material: Polyester (yarn C, Table II)	
Distance from impact point to clamp	$L = 155.0$ cm.
Camera speed	15,444 frames/sec.
Transverse-impact velocity	$V = 40.0$ m./sec.
Initial transverse-wave-front velocity	$\bar{U}_1 = 135.3$ m./sec.
Final transverse-wave-front velocity	$\bar{U}_2 = 219.2$ m./sec.
Impact occurs at	frame 6.70
Velocity apparently changes from $\bar{U}_1$ to $\bar{U}_2$ at	frame 22.33
when $t_i = (22.33 - 6.70)/15{,}444$	$= 1.012 \times 10^{-3}$ sec.
and	$d_i = 13.69$ cm.
Approximate strain-wave velocity $C = \frac{2L}{t_i}$	$= 3063$ m./sec.
$\frac{V}{C} = 0.013$ so that from Equation 8	$\epsilon_1 = 0.0019$
Least possible value of strain-wave velocity $C = [2L(1 + \epsilon_1) - d_i]/t_i(1 + 2\epsilon_1)$	$= 2922$ m./sec.
Greatest possible value of strain-wave velocity $C = [2L(1 + 3\epsilon_1) + d_i]/t_i(1 + 2\epsilon_1)$	$= 3203$ m./sec.
Upper limit for $\bar{U}_2$	$1.50\ \bar{U}_1 = 203$ m./sec.
Corresponding lower limit for C (found by trial and error)	$C_1 = 2985$ m./sec.
Lower limit for $\bar{U}_2$	$0.88\ \bar{U}_2 = 192.9$ m./sec.
Corresponding upper limit for C (found by trial and error)	$C_2 = 3024$ m./sec.
Estimated value of C	$C_1 + \frac{2}{3}(C_2 - C_1) = 3011$ m./sec.

known and the wave length λ has been determined, the velocity C can be found from the formula

$$C = \lambda\nu \tag{17}$$

Velocities determined in this way are usually higher than velocities calculated from Equation 1 using slow-speed tension–strain data. Frequencies used in the measurement lie in the range 5000–25,000 c.p.s., and data by Fujino [3,4] demonstrates that velocities measured are constant over this range of frequencies.

If the amplitude of vibration of the induced strain wave is A_0, the maximum velocity at which the particles of the yarn vibrate is $2\pi\nu A_0$. Thus for an amplitude of 10^{-4}m. the particle velocity ranges from $2\pi \times 5000 \times 10^{-4}$ to $2\pi \times 25{,}000 \times 10^{-4}$ or 3–15 m./sec. depending upon the frequency. In the case of the transversely impacted yarn discussed previously, the particle velocity given by Equation 2 is $C\epsilon$ or $3000 \times 0.002 = 6$ m./sec. As the particle velocities for these two methods are of the same magnitude, the strain wave velocities measured by each method should be comparable.

Results and Discussion

Strain wave velocities were measured on each of the textile yarns described in Table II. These yarns are representative of commercial production of the years 1952–53. In order to help characterize the yarns, the tenacities at break, breaking elongations, and initial moduli, obtained at a testing rate of 10%/min., are also given.

The strain wave velocities were obtained in three different ways. First, the tension–strain curves for the yarns were obtained at a testing rate of 100%/min. The initial slope of each curve was used as a datum in Equation 1 for the calculation of C. To obtain the tension–strain curves, tests were made on at least 5 10-in. specimens from each yarn sample. Some of the samples were given an additional twist of 2 turns/in. before testing in order to prevent strand-by-strand breakage. The values of C obtained by this method are given in the first column of Table III.

The sonic modulus technique of Ballou and Smith described in the preceding section was also used to measure C for each of the textile yarns. The oscil-

TABLE II. Description of Yarns Tested *

A. Acetate, bright, 16.7 tex, 16 filament 10.8/35.6/340

B. Triacetate, 16.7 tex, 40 filament 11.8/24.7/405

C. Polyester, bright, 7.8 tex, 34 filament, 42.6/24.8/990

D. Glass fiber, 34 tex, 204 filament, 1 Z twist 50.2/2.5/2340

E. Rayon, high tenacity deacetylated cellulose acetate 30 tex, 3 ply, 2.5 Z twist (90 tex total) 61.2/6.4/2030

F. Rayon, high tenacity deacetylated cellulose acetate (experimental) 88.9 tex, 1392 filament, 2.5 Z twist 61.1/5.6/2250

G. Rayon, high tenacity, 183.3 tex, 1100 filament 28.5/8.1/880

H. Nylon, bright, high tenacity, 23.3 tex, 5 ply, 3 Z twist (117 tex total) 60.8/17.6/370

I. Nylon, bright, high tenacity 93.3 tex, 140 filament, 0.5 Z twist 68.9/15.8/410

J. Nylon, undrawn monofil, variable tex approximately 155 7.64/376/93

K. Nylon, undrawn multifil, 109 tex, 34 filament, 6.64 g./tex at 300% elongation, 82 g./tex initial modulus

L. Acrylic, semi-dull, 16.7 tex, 80 filament 44.6/18.1/870

M. Saran, 22.2 tex, 12 filament, 1 Z twist 19.5/19.5/122

N. Braided silk fish line, 24 lb. test, approximately 310 tex, 34.3/18.8/414

* As an aid in characterization, the physical properties of the above yarns are given in the form A/B/C where A is the breaking tenacity expressed in grams per tex, B is the breaking elongation expressed in percent, and C is the initial slope of the tenacity–strain curve expressed in grams per tex. These values were obtained from tests performed with a commercial tester at 10%/min. constant rate of straining.

TABLE III. Strain Wave Velocity C, by Three Different Methods

Sample	C from initial slope of tension-strain curve, m./sec.	C from transverse impact measurements, m./sec.	C from sonic-modulus method [1], m./sec.
Acetate (A)	1900	1920	2050
Triacetate (B)	2100	2170	2250
Polyester (C)	3280	3050	3280
Glass fiber (D)	4960	4680	5040
Rayon (E)	4840	4640	5150
Rayon (F)	5180	5070	5270
Rayon (G)	3140	3260	3270
Nylon (H)	2000	2210	2370
Nylon (I)	2110	2400	2490
Nylon (J)	1030	1440	1340
Nylon (K)	930	1440	1340
Acrylic (L)	3100	3480	3620
Saran (M)	1140	1830	2640
Silk (N)	2180	2010	2650

lation frequencies used in this method ranged from 7000 to 24,000 cycles/sec. Results obtained with at least three different frequencies on each yarn were averaged to obtain the value reported. Tensioning weights just sufficient to keep the yarn taut were used. In most cases the tensioning force was less than 1 g./tex. It was necessary to use several plies of the lower tex samples in order to get a good signal from the detecting crystal, but the plies were not twisted together. The values of C obtained by this method are given in the last column of Table III.

A number of impact tests was performed on each yarn sample. Data from these tests are given in Table IV. In the tests the distances from the central impact point to either clamp ranged from 112 cm. to 185 cm. depending upon the sample tested. In order that the yarn specimen used could be seen on the photographic record, it was necessary to ply some of the yarns as many as 20 times. The plied specimens were given a small twist to prevent the plies from spreading after the impact. The transverse-impact velocities were usually near 40 m./sec. in magnitude, although in two instances velocities near 60 m./sec. were used. The impacting missile was a steel rod about 3 in. long weighing approximately 30 g. The end of the rod was grooved to engage the specimen upon impact.

The velocities of the transverse-wave front $\bar{U}_1$ before interaction with the returning strain wave pulse are given in Table IV. Also tabulated are the transverse-wave-front velocities $\bar{U}_2$ which result after the strain-wave pulse has returned from the clamp, interacted head-on with the transverse wave, been reflected at the missile, and again overtaken the transverse-wave front. In the last column of Table IV are tabulated the values of the strain-wave propagation velocity C. These values of C were calculated according to the method outlined in the preceding sections.

TABLE IV. Impact Tests on Textile Yarns *

Sample	$\frac{1}{2}L$, cm.	Ply/twist†	V, m./sec.	$\bar{U}_1$, m./sec.	$\bar{U}_2$, m./sec.	C, m./sec.
Acetate (A)	140	10/–	46.1	130	196	1940
	125	8/0.5 S	41.5	122	189	1900
Triacetate (B)	140	10/–	44.1	139	202	2200
	130	10/0.5 S	40.5	120	191	2140
Polyester (C)	150	16/–	44.4	165	243	3100
	155	20/0.5 S	40.0	135	219	3010
Glass fiber (D)	160	8/–	42.7	163	262	4620
	160	8/–	41.8	159	258	4750
Rayon (E)	160	as is	43.0	171	282	4690
	160	as is	43.7	166	271	4600
Rayon (F)	160	as is	43.8	174	285	5040
	160	as is	42.5	170	269	5110
Rayon (G)	160	as is	44.0	149	232	3120
	170	as is	41.0	144	218	3400
Nylon (H)	138	as is	42.9	143	212	2340
	138	as is	43.5	131	196	2280
	138	as is	38.4	132	185	2160
	138	as is	35.4	125	181	2210
	138	as is	61.7	162	249	2150
	138	as is	61.3	153	237	2110
Nylon (I)	138	2/–	43.9	149	226	2390
	138	2/–	43.1	142	216	2400
Nylon (J)	112	4/–	43.4	114	170	1440
Nylon (K)	140	2/–	44.0	115	167	1440
Acrylic (L)	150	10/–	44.6	153	227	3510
	185	10/0.5 S	40.9	161	234	3440
Saran (M)	140	10/–	43.5	115	166	1790
	125	10/0.5 S	36.6	102	150	1790
	155	10/0.5 S	39.5	119	164	1910
Braided silk (N)	139	as is	42.9	117	180	1650
	139	as is	40.8	127	207	1870
	170	as is	41.5	127	183	2150
	125	as is	40.8	129	192	2110
	125	as is	40.6	118	186	2260

* $\frac{1}{2}L$ is the distance from impact point to clamp, V is the transverse impact velocity, $\bar{U}_1$ is the velocity of the transverse-wave front just after impact, $\bar{U}_2$ is the velocity of the transverse-wave front after the head-on and overtaking interactions with the strain-wave pulse, and C is the strain-wave propagation velocity.

† The units are: number of plies/turns per centimeter.

From Table IV it is seen that each impact test was performed at least two times on all but the undrawn nylon samples. In most cases the values obtained for C agree within a few percent. It is possible that effects may exist due to differences in ply and twist and in the static tension used in the tests. The distance from impact point to clamp might also have an effect. It seems, however, that under the conditions used in this investigation these effects were small, except in the case of braided silk. In the five specimens of this material that were tested the values of C obtained ranged from 1650 to 2260 m./sec. This is probably an effect of the braided structure. When the specimen is slack the structure is loose and open. The initial slope of the tension–strain curve has a low value representative of the braided structure rather than of the silk filaments. At higher strains and tensions the structure becomes tight and compact. The slope of the tension–strain curve is steeper and more representative of the properties of the silk itself. Therefore the velocity of a strain wave propagating along the braid would depend sensitively in this case upon the static tension applied before impact.

The values of $\bar{U}_1$ and $\bar{U}_3$ are tabulated to show the order of magnitude of the transverse-wave-front propagation velocity. The value of $\bar{U}_1$ depends upon the value of the transverse impact-velocity used in the test, increasing or decreasing as V increases or decreases. This dependence between $\bar{U}$ and V is borne out in Table IV except in a few instances. The effect of static tension upon the velocity $\bar{U}_1$ is probably responsible for these anomalous cases. The values of $\bar{U}_3$ are higher than $\bar{U}_1$, but the ratio $\bar{U}_3/\bar{U}_1$ never attains the theoretically maximum value of $(\bar{U}_2/\bar{U}_1) \times (\bar{U}_3/\bar{U}_2) = 1.50 \times 1/0.88 = 1.71$. The low values of $\bar{U}_3/\bar{U}_1$ are partly due to the static tension which raises the value of $\bar{U}_1$ and partly due to attenuation of the strain pulse.

Table III compares the strain-wave velocities obtained by the three different methods. Before these data were tabulated it was expected that the values of C calculated from initial slopes of the tension–strain curves would be lowest. The velocities C measured from transverse impact and by the sonic-modulus technique were expected to be higher and comparable in value. These expectations were borne out in most cases. However, values of C measured by the transverse-impact technique were lower than the values of C computed from the slope of the tension–strain curve in the cases of polyester, glass fiber, rayon (E, F) and silk. Some of this discrepancy may be attributed to inaccuracies in measurement. The variation in impact results obtained by different measurements on a yarn sample may be seen in Table IV. The results tabulated for nylon (H) are typical.

In the case of saran the velocity obtained from impact measurements is much greater than the velocity obtained from tension–strain data and much less than the velocity measured by the sonic-modulus technique. This unexpected result cannot be explained on the basis of the present data. For silk the velocity obtained from impact measurements was much less than the velocity obtained by sonic-modulus measurements. Here, however, the strain was propagated along the braided structure in the impact tests and propagated along the individual silk fibers in the sonic tests. Thus the velocities obtained by the two methods would be expected to differ.

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Sorption Kinetics of Water Vapor in Wool Fibers: Evaluation of Diffusion Coefficients and Analysis of Integral Sorption

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Abstract

A number of interval sorption experiments have been made and analyzed, assuming Fick's law; diffusion coefficients were derived. These coefficients have been used to predict the behavior in integral sorption; the disagreement between prediction and experiment is discussed. Integral sorption experiments have also been carried out on horse hairs of various diameters to trace the influence of diameter on the sorption rate.

General

The general shape of the water sorption curve by wool for small changes of relative humidity is well known [11, 22]; it is very similar to those for water in cellulose [8, 20] and for organic vapors in cellulose acetate [2]. These curves may best be described in terms of a two-stage sorption process in which the first stage corresponds to Fickian diffusion and the second stage to a further uptake of sorbate the rate of which is not controlled by diffusion but by a molecular relaxation process of the sorbent. The exact nature of this relaxation process is not yet fully understood, although an approximate calculation [2] has shown that it may be due to the relaxation of the elastic strain imposed on the polymer network by the volume swelling accompanying the first stage of sorption.

In an attempt to analyze the observed kinetics of water sorption by wool, perhaps the most outstanding feature which requires explanation is the difference in the form of the uptake curves for small and large steps in relative humidity. In the absence of a more appropriate theory, an analysis in terms of Fick's law has to be undertaken. It has been shown by Crank [5] that, at least qualitatively, the major characteristics of the sorption behavior of many polymer systems can be explained in terms of Fick's law provided the diffusion coefficient is made a function of (a) the concentration, (b) the time, and (c) the strain set up in the sorbent.

The only available data for diffusion coefficients which may be applicable to the wool–water system have been reported by King [17] for horn keratin using a steady-state permeability method. King found that the steady-state diffusion coefficient was a function of the concentration of the water in the keratin and published the curve relating regain and diffusion coefficient. Unfortunately, the physical form of the wool fiber makes it impossible to devise a steady-state experiment by which the concentration dependence of the diffusion coefficient can be measured. One is forced, therefore, to approximate the required conditions of the measurement by making the step of concentration as small as possible and assuming that, over the small range used, the coefficient is constant. This type of experiment, however, does not rule out time or strain effects.

The small-step sorption experiments reported here were undertaken with a twofold purpose in view: to check whether agreement could be obtained between diffusion coefficients for wool keratin and King's published figures for horn keratin and to find to what extent the sorption and desorption curves predicted by the concentration-dependent diffusion coefficients [16] fall short of the observed behavior.

Diffusion coefficients and integral sorption curves for wool have been measured in this laboratory by another method, that of direct gravimetric determination in a vacuum apparatus with only water vapor present [23]. The vacuum apparatus yields rates of uptake which are considerably slower than those found by us. Detailed instances where substantial differences exist are indicated in this paper by foot-

notes. The reason for the differences is not known at present.

Interval Sorption

All the small-step interval measurements reported in this section were made on the same wool fiber, which was a Corriedale of 49.4×10^{-4} cm. dry diameter. The sensitivity of the vibroscope used [10] was such that a regain change of 1% gave full scale deflection on the recorder chart (28 cm.); the chart speed was 4 in./min. Measurements were made at 35°, 25°, and 5° C., the temperature in each case being controlled to ±0.02° C. Altogether 25 steps of 2% humidity were taken ranging from 50 to 100% relative humidity. The general procedure was to dry the fiber for about three days in a stream of air which was passed over concentrated H_2SO_4. Then the humidity was changed slowly from 0 to 50% in the course of 24 hr. On reaching 50% relative humidity discrete relative humidity changes were made, allowing at least 24 hr. in each case for equilibrium to become established (within the accuracy of measurement) before making the next change.

The initial portion of a typical uptake curve is shown in Figure 1, where increase in regain is plotted against time. The same curve (extending over a longer period) is shown in Figure 2 plotted against the square root of time. The particular interest here is in the first stage of sorption, which was found to resemble very closely Fickian diffusion into a cylinder with a constant diffusion coefficient (dotted line in Figure 1).

This shape did not seem to change over most of the range investigated. It was thus possible to fit Fickian curves to the experimental results and derive the values of the diffusion coefficient at the appropriate concentrations. In fitting the curves, the expression

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n{}^2} e^{-D\alpha_n{}^2 t}$$

for diffusion into a cylinder was used [7], where M_t = amount of water sorbed at time t by a cylindrical fiber of radius a and diffusion coefficient D; M_∞ = amount of water sorbed at equilibrium, which in this analysis is taken to mean the end of the first stage of sorption; and α_n = nth root of $Jo(a\alpha_n) = 0$ where $Jo(x)$ is the Bessel function of the first kind of order zero. This expression may be plotted as a function of M_t/M_∞ against (D_t/a^2) and the scales of the ordinate (M_t/M_∞) and the abscissa (D_t/a^2) changed independently until the best fit to the experimental curve is obtained. Then, sim-

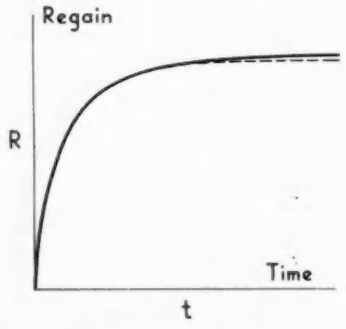

Fig. 1. Initial portion of a typical sorption curve for a small step in regain. The dotted line represents Fickian diffusion into a cylinder with a constant diffusion coefficient.

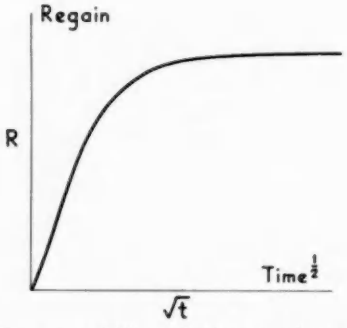

Fig. 2. The curve of Figure 1 plotted against square root of time.

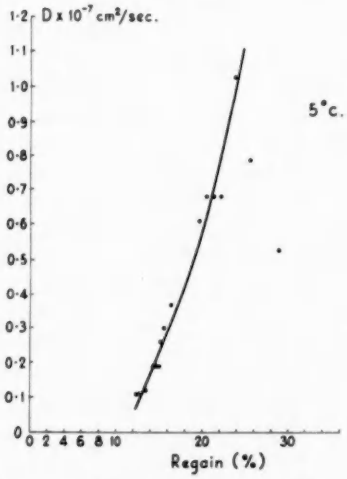

Fig. 3. Values of diffusion coefficient obtained at 5° C.

ply by comparing the scales of the recorder trace and the theoretical curves, the unknowns M_x and (D/a^2) can be found.

Figures 3, 4 and 5 contain plots of diffusion coefficients thus found.[1] There is quite a large scatter of the experimental points, but this is not primarily due to a difficulty in obtaining an accurate fit between the observed and Fickian diffusion curves but rather due to a lack of consistent results in consecutive measurements. There are several interesting features to be noted. First, there does not appear to be a very large temperature dependence. Also, at all three temperatures the apparent diffusion coefficient decreases again with concentration above about 25% regain (at relative humidities greater than 94–95% RH), and at still higher regains (greater than 30%) it was found that the initial portion of the observed uptake curve no longer had the shape expected for Fickian diffusion. Finally, on Figure 4 for 25° C., the diffusion coefficient versus concentration relationship reported by King [17] is given for comparison and a general agreement over the concentration range investigated is found.

[1] Values of diffusion coefficient found by the present method are substantially greater than those reported by Watt [23] using a gravimetric method and a vacuum apparatus. For example, over the regain range 12–21%, at 35° C., diffusion coefficients found by the vibroscope method are 6–16 times greater than those found with the vacuum apparatus.

Theoretical Appraisal of Integral Sorption

It is of great interest, in the case of wool, to make a calculation of the expected sorption and desorption curves for large relative humidity steps, based solely upon a concentration-dependent diffusion coefficient, in order to assess what the rate-governing process might be. For this purpose a purely empirical relationship between diffusion coefficient and regain was chosen (shown in Figure 5) to represent the experimental data. This relationship was then used to

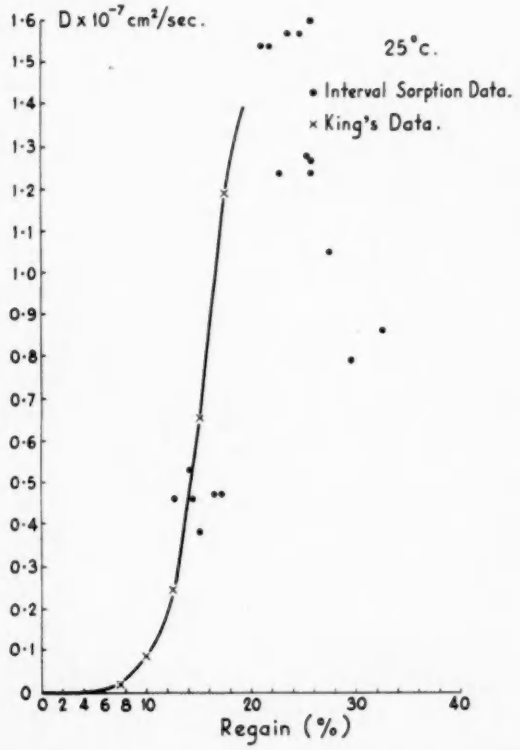

Fig. 4. Values of diffusion coefficient obtained at 25° C. together with those obtained by King at the same temperature for horn keratin.

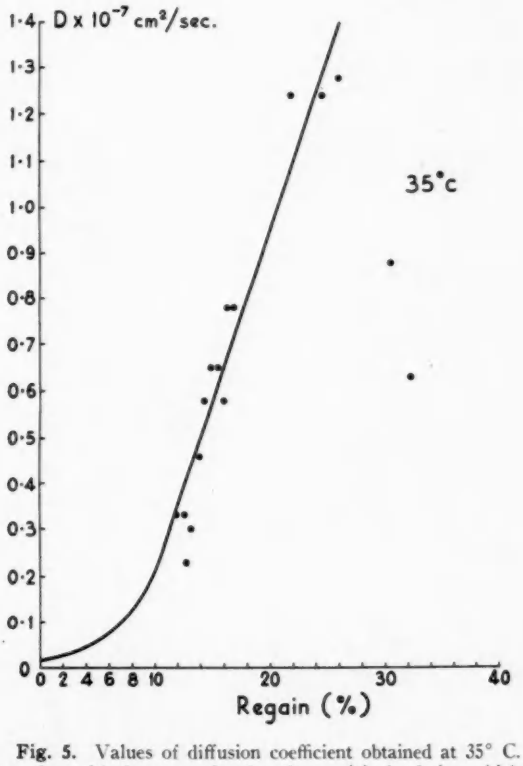

Fig. 5. Values of diffusion coefficient obtained at 35° C. together with the curve showing the empirical relation which was used in the theoretical calculation of a typical integral sorption step.

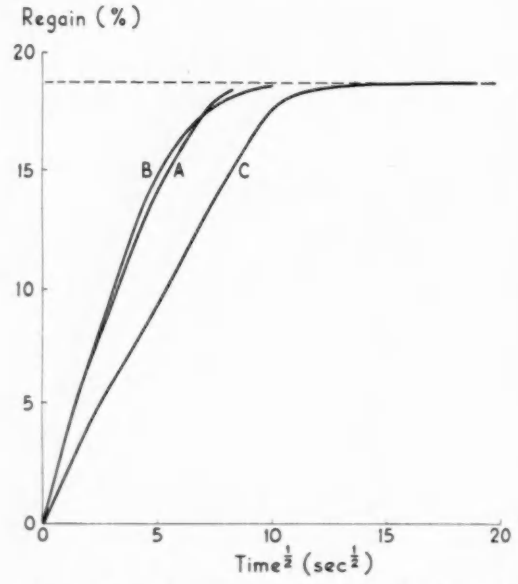

Fig. 6. Theoretical and experimental sorption curves for a step from 0 to 80% relative humidity. A—theoretical curve based on a concentration-dependent diffusion coefficient. B—theoretical curve based on a constant diffusion coefficient representing an average value. C—experimental curve.

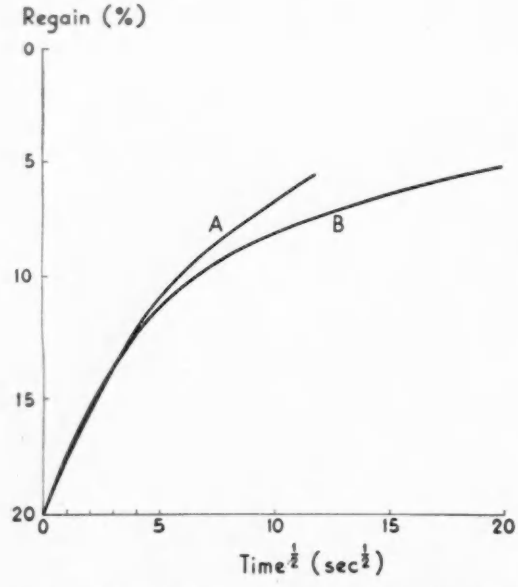

Fig. 7. Theoretical and experimental desorption curves for a step from 80 to 0% relative humidity. A—theoretical curve based on a concentration-dependent diffusion coefficient. B—experimental curve.

calculate the absorption and desorption curves for a 0–80% step in RH (0–18.8% regain) at 35° C. by use of the method of finite differences [7].

The results of the calculation for absorption and desorption are shown in Figures 6 and 7 where the moisture gain or loss is plotted against the square root of time. In Figure 6 is also plotted a Curve C, representing an experimental result under the same conditions. The theoretical Curve A lies above Curve C,[2] although the two rates of uptake are not greatly different. The characteristic feature of the experimental curve is that it consists for the most part of an almost straight line passing through or near the origin. (Sometimes a small "foot" or initial region of increasing slope is observed in the experimental curve, and sometimes an "overshoot" at the upper end, especially at the higher temperature of 35° C.; these features were not apparent in the particular curve shown here.) Curve B in Figure 6 represents Fickian diffusion with a constant diffusion coefficient, given by

$$\bar{D} = \frac{1}{C}\int_0^c D(c)dc$$

where $D(c)$ is the empirical relation between D and C which has been employed. Comparison of Curves A and B indicates that the concentration dependence of the diffusion coefficient does not much alter the shape of the absorption curve for a cylinder except to make it somewhat more linear (in square root of time) with a sharper bend towards the end of the process.

In the case of desorption there is a fair agreement between the theoretical Curve A and the experimental Curve B, particularly in the initial slopes, although later in the process the experimental curve becomes slower than the theoretical one. A similar agreement for desorption has been found by Haly and Roberts [16], who used King's data on horn keratin for the diffusion coefficient and compared the calculated curves with their experimental results obtained using thin layers of wool fibers. In the

[2] The shape and initial slope of the integral uptake curve found by the present method differ from the behavior found using a gravimetric method and a vacuum apparatus [22]. For example, in a step from 0 to 80% RH at 35° C. the initial slope using the vibroscope method is twice as great as with the vacuum apparatus, and the times taken to reach equilibrium are 3 min. and 20 min. respectively. Agreement with the vibroscope result has been obtained in a weighing experiment in air using a bulk wool sample [19].

case of absorption, however, Haly and Roberts found that the theoretical curve predicted a much faster rate than that actually obtained by experiment (using Merino fibers).

Unfortunately, it is not possible to accept any but major differences between the theoretical curve and the experimental ones as evidence in the interpretation of the kinetic behavior. The reason for this is twofold. First, as mentioned previously, the experimental data can not be reproduced exactly. This is probably due to differences in the history of the sample prior to the experiment the effects of which on the sorption rates are still to some extent unknown. Second, there arises an uncertainty on theoretical grounds as to the correct diameter of fiber to use in the computation. Apart from diameter variations along the fiber, there is also a change due to swelling as water is absorbed or lost. It is doubtful when calculating diffusion coefficients at various regains whether one ought to use the unswollen or swollen diameter. If the absorbed water in the wool fiber is thought to be localized on sites and if diffusion takes place by jumps from site to site, then on an average a water molecule will reside longer on a site than in the process of jumping. A swelling of the molecular network increasing the distance between sites will, therefore, not increase the time for the diffusion by the same proportion. On the other hand, the introduction of water molecules on swelling may increase the total number of sites or alter the time for which a molecule stays at a site, so that the net time for diffusion may increase. The exact value to use for the diameter in calculating diffusion in a swelling structure of changing composition is, therefore, uncertain.

Effect of Diameter Variations on Integral Sorption

Apart from the uncertainties regarding the diameter of the swollen fiber for diffusion calculations, it is of interest to investigate the influence on the sorption rates of varying the diameter of the dry fiber. Crank [5] and Park [21] investigated the effect which a time-dependent diffusion coefficient has on the sorption rates for various thicknesses of sheet of polymer films in systems such as methylene chloride–polystyrene. These authors were able to show that Fickian diffusion based on a constant or on a concentration-dependent diffusion coefficient, which requires that the time of diffusion alters as the square of the thickness of the film, no longer represented the data and that, at least qualitatively, the experimental results could be explained if the diffusion coefficient were made to depend on time. To perform a similar test for the keratin–water system, a white horse hair, originally of a diameter of 187μ (dry), was ground in successive stages to 160μ, 117μ, and 87μ diameter. (Our thanks are due to J. Snaith of this laboratory for carrying out this delicate operation.) Sorption and desorption experiments (0–80% RH steps) were performed on the original fiber and after each successive cut. The resulting sorption curves normalized for small differences in the final equilibrium uptake are shown in Figure 8. The quantity $\sqrt{t/a^2}$ was plotted along the abscissa so that for Fickian diffusion with a concentration-dependent diffusion coefficient all four curves should coincide. The curves do not show this behavior, and the deviation appears to be systematic in the sense predicted by Crank for a diffusion coefficient which increases with time: that the thickest fiber has relatively the fastest sorption rate. All four curves show a "foot" at the beginning, then a long straight portion, and finally a rapid approach to equilibrium near the top end. The sorption rate of the Corriedale fiber (49.4μ diameter dry) used in the work on interval sorption has been given on the same figure as comparison. It is seen that ex-

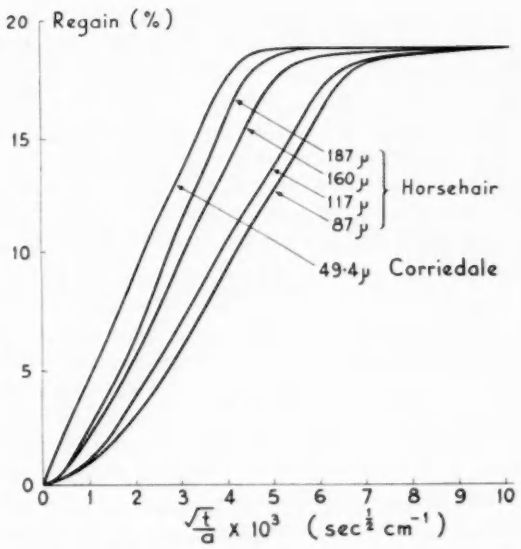

Fig. 8. Comparison of sorption curves (0–80% relative humidity) for a horse hair progressively ground to smaller and smaller diameters.

cept for the "foot" the uptake rate is similar to those of the horse hair, although it does not give the rate expected for its diameter. This indicates that the variation in behavior between a horse hair and a Corriedale fiber appears to outweigh the diameter effect; i.e., results using a 187μ horse hair and a 49.4μ Corriedale fiber are comparable; the failure of the keratin–water system to obey the time–diameter squared relationship is not a gross one.

Discussion

In other papers [11, 19, 22, 23] a large mass of experimental data has been presented for the sorption kinetics of the wool–water system. It must be the ultimate aim of such a kinetic study to lead to a coherent theory capable of explaining the observed rates in terms of molecular mechanisms and the specific properties of the systems. For the present system, no comprehensive theory exists; this paper examines the data in the light of existing theories to find to what extent agreement is obtained.

The simplest case of diffusion is covered by Fick's law, in which the driving force for the transport of matter is simply a concentration gradient (or entropy increase which the system is capable of undergoing). Such a simple law is not applicable to the present system. The next refinement is that of making the diffusion coefficient a function of concentration. This is a mathematical device, which covers two distinct physical phenomena. First, an increase in concentration of the sorbate causes a swelling of the sorbent, leading to an expansion of the molecular structure. This may facilitate the transport of material and thus increase the diffusion coefficient. A similar process active in diffusion-controlled stress relaxation in polymers has been called the "plasticizing effect" by Fujita and Kishimoto [13]. Second, if the sorbate diffusing into the sorbent is held by sites of varying energies, then the driving force for diffusion contains an energy factor which depends on concentration. Thus, if instead of the normal diffusion where the flow of material F is proportional to the concentration gradient

$$F \propto \frac{\partial c}{\partial x}$$

one introduces another function, K, the effective concentration (that is, the concentration gradient weighted by a factor to allow for varying degrees of binding to sites depending on their energies) and K is a function of concentration itself, then

$$F \propto \frac{\partial K(c)}{\partial x}$$

The ordinary linear diffusion equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\,\frac{\partial c}{\partial x}\right)$$

is then replaced by

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\,\frac{\partial K(c)}{\partial x}\right)$$

If

$$\frac{\partial K(c)}{\partial x} = \frac{\partial K(c)}{\partial c} \times \frac{\partial c}{\partial x}$$

then

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\,\frac{\partial K(c)}{\partial c} \times \frac{\partial c}{\partial x}\right)$$

or

$$= \frac{\partial}{\partial x}\left(D(c)\,\frac{\partial c}{\partial x}\right)$$

It can thus be shown that sites of varying energy in the sorbent lead mathematically to a concentration-dependent diffusion coefficient. This idea has been used by King [17] to predict the diffusion coefficient for horn keratin from theoretical considerations. King, however, did not take into account any contribution to the concentration dependence from the "plasticizing effect."

It has been shown earlier in this paper that King's concentration-dependent diffusion coefficient is supported by the experimental results from interval sorption and that calculations based on the concentration-dependent diffusion coefficient are in reasonable agreement with the experimental results. However, the agreement may be largely fortuitous, particularly in view of the fact that the long linear portion of the uptake curve is not predicted, that the sorption rate is slower than predicted, and that the required diameter relationship is not observed.

One may, therefore, proceed with the further elaboration of making the diffusion coefficient time-dependent. If this is done, then at least qualitatively the shapes of the uptake curves and also the diameter relationship can be explained [4]. Unfortunately, however, the choice of the time function is almost completely arbitrary, and to proceed simply by finding the function which will give the best agreement

with experiment will not necessarily give much insight into the mechanism controlling the sorption rates. The procedure also suffers from the defect that it does not include an explanation for the small-step, two-stage sorption.

It appears more fruitful to examine the influence of stress on the sorption behavior. In general, the elastic properties of the swelling material will tend to oppose entry of the sorbent and, according to the picture developed particularly by Barkas [3], Cassie [4], and Newns [20], the uptake of water at any stage of the process leads to the establishment of an equilibrium between water content and swelling stress. In the typical two-stage process observed in interval sorption, the initial stage tends to expand the protein network of the wool matrix elastically. During this process, the rate is similar to that predicted by Fick for a cylinder with a constant diffusion coefficient, provided the concentration increase is sufficiently small [19]. This is borne out by the evidence obtained from the present experimental work. At the end of the first stage a further uptake of water can be distinguished which can be attributed to a relaxation of stress of the molecular network, altering the free energy balance. The rate of this process is no longer diffusion controlled but stress–relaxation controlled; the process is much slower and takes place with an essentially uniform concentration of water throughout the fiber.

Experimental evidence [19] from results of further vibroscope studies shows that as the step in relative humidity is made bigger and as it is made at a higher regain, the speed of the molecular relaxation process is increased until finally its rate becomes comparable with that of the diffusion process. The acceleration of relaxation may result from a cooperative action of water molecules when a number of adjacent sites become occupied at the same time and the localized "swelling" processes combine.

Similar behavior is observed in desorption [19]. Comparison between a series of interval desorption curves and an integral desorption curve shows that, whereas in interval desorption a considerable proportion of the water lost is released at a very slow rate (during the second stage), in integral desorption most of the water is removed very rapidly. It appears, therefore, that the abrupt removal of a large amount of water from the fiber brings about an acceleration of the long-term processes involved, the mechanism probably being a cooperative action such as has already been mentioned in connection with integral sorption.

A point of difference between the integral sorption and desorption curves is that in the former the whole of the second-stage relaxation processes become accelerated to rates comparable with those of the first stage; in integral desorption, however, some of the characteristically slow second-stage behavior always remains. The probable explanation lies in the different patterns of water distribution within the fiber in the two cases (estimated by Haly [15], illustrated approximately in Figure 9). An earlier interpretation of the effect was in terms of differential stress [11], but the following explanation seems more probable. In integral sorption a pronounced gradient of water concentration moves inward [14, 15] so that successive regions of the fiber are subjected to an abrupt increase in concentration, which has the accelerating effect on relaxation already mentioned; this behavior persists until the gradient reaches the fiber axis. In integral desorption no moving boundary exists [15]; except at the fiber surface the water distribution is approximately uniform. In the early part of desorption the water content throughout falls rapidly, giving rise

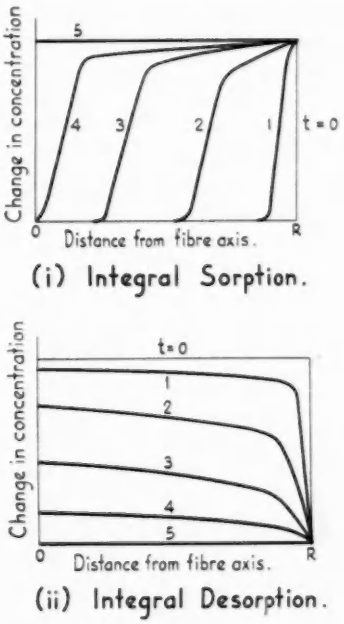

Fig. 9. Comparison of concentration profiles for sorption and desorption—schematic.

to effects of accelerated relaxation. As desorption approaches completion, however, the rate of change of regain everywhere falls to an extent such that acceleration does not occur; the situation in the fiber is then the same as at the beginning of an interval desorption step, and the characteristic slow second stage is observed.

There is, however, still no explanation of two features of the integral uptake curves which are observed. One is the long linear portion of the uptake curve (on a square root of time plot) which characterizes the typical integral step from low regains. The other is the fact that the observed uptake curves are slower than those predicted theoretically. One would assume that if all that took place by increasing the size of step was a speeding up of the molecular relaxation, then the observed curves, in the limit, should either be as fast as the theoretical ones or faster, but never slower. The possibility of a third process taking place during integral sorption therefore cannot be excluded.

It has been noted in this laboratory [18] that, for typical integral sorption steps, the torsional rigidity undergoes a very marked change. In the first few minutes it drops rapidly, passing through a minimum, and then it builds up again slowly. This drop in torsional rigidity corresponds to a weakening in the structure of the matrix of the wool fiber and has been interpreted by Feughelman [12] as due to the formation of a temporary sol state in which hydrogen bonds are weakened or broken during the rapid water uptake. The bonds subsequently reform slowly to form a gel-like structure [1]. The possibility must not be ruled out that the rate-controlling process during typical integral steps may be controlled to some extent by this phenomenon.

It may also give an explanation why sometimes "overshoots" of regain are observed. A change of the structure due to re-formation of hydrogen bonds may be accompanied by a decrease in water content. In cases where no overshoot is observed, it has been reported previously by Downes and Mackay [11] that a typical integral step places the system on the desorption branch of the isotherm or somewhere inside the hysteresis loop, but not on the absorption branch. The "overshoot" therefore may only be a special case in which the instantaneous water content is so great as to lie above the absorption branch or even outside the desorption branch of the isotherm.

The phenomenon of molecular stress relaxation during the second stage of interval sorption, which takes place at essentially constant water content, should not be confused with another type of stress relaxation due to the geometry of the swelling material. The stress involved here is that set up by the differential swelling occurring during diffusion and which is high during the initial stages. During absorption, for example, the very first water entering the structure is assumed (as a boundary condition in the solution of Fick's diffusion equation) to bring the outer layer of the fiber to the final equilibrium water content instantaneously. This would require a swelling of up to about 30% of the volume of the outer layer. This swelling will to some extent be hindered by the core of the fiber which is still unswollen; hence initially the uptake rate will be somewhat slower than the predicted one. A similar argument may be used to show that an effect of this kind would tend to make the initial rate of desorption faster than that predicted theoretically [9]. It is difficult to estimate the magnitude of this effect and to ascertain whether it could be responsible for the "feet" in the uptake curves which are observed sometimes.

The lack of an explanation of the integral sorption kinetics for changes starting from dryness in terms of simple diffusion theory leads to speculation about other possible models. The predicted uptake curves, taking into account the concentration dependence of the diffusion coefficient, are faster than those observed experimentally. This suggests that there may exist a slower rate-limiting process superimposed on the diffusion process. At this stage one may only speculate as to the nature of such a process. One very simple mechanism which one may consider is that in which there is a finite velocity which limits the rate at which the hydrogen bonds of the wool may be broken (dissolved). In general, if one assumes that transport of water (by diffusion) to the site of the unbroken hydrogen bonds is not the limiting factor, then the over-all rate of breaking will be proportional to the number of such bonds exposed. It is well known [14] that for the type of sorption step considered here the water penetrates the wool fiber with a well-defined front; hence it may be stipulated that the rate of hydrogen bond breakage is proportional to $2\pi r$, where r is the radius of the cylinder defining the position of the front at any time t.

Or

$$s = 2\pi kr \qquad (1)$$

where k is a constant and s the limiting reaction rate between the penetrant water and the existing hydrogen bonds. One also obtains for the reaction rate

$$s = C\frac{\delta V}{\delta t}$$

where C is the volume concentration of the water behind the front and δV the volume swept out in time δt.

$$\therefore \quad s = \pi Cl\frac{d}{dt}(R^2 - r^2)$$

where l is the length of the cylinder and R the outer radius of the fiber.

$$\therefore \quad s = -2\pi Clr^2\frac{dr}{dt} \qquad (2)$$

From Equations 1 and 2 it is seen that dr/dt is a constant (negative because r decreases as t increases). Hence the assumption of a constant reaction velocity leads to a front penetrating at a constant velocity. If this velocity is given by V and the time required for the front to penetrate from the surface to the center of the fiber by t_f, it can be shown that

$$\text{regain} \propto 2\pi VR\left(t - \frac{t^2}{2t_f}\right)$$

A plot of the relationship on a time$^{\frac{1}{2}}$ basis is shown in Figure 10; it is seen that it exhibits the essential features of an integral uptake curve although the "foot" is more pronounced than observed experimentally.

It is also a feature of this model that for fibers of different diameter the times required to reach a given regain do not vary as the square of the diameter as required by the diffusion theory, but directly as the diameter. A comparison on this basis is made in Figure 11, where the results from the horse hair experiment are plotted as a direct diameter relationship; closer coincidence between the curves is obtained than is the case in Figure 8.

It appears fairly clear at this juncture that future progress in this work will probably be derived from a study of what may be called stress–relaxation controlled diffusion and also possibly from a more detailed study of the sol-gel transformation observed during very fast changes in regain.

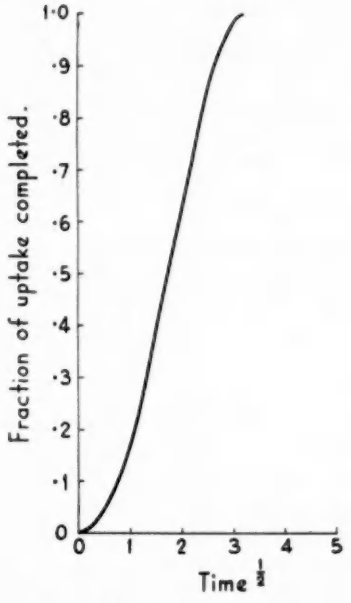

Fig. 10. Theoretical sorption curve for a cylindrical fiber in which the concentration front advances with a constant velocity.

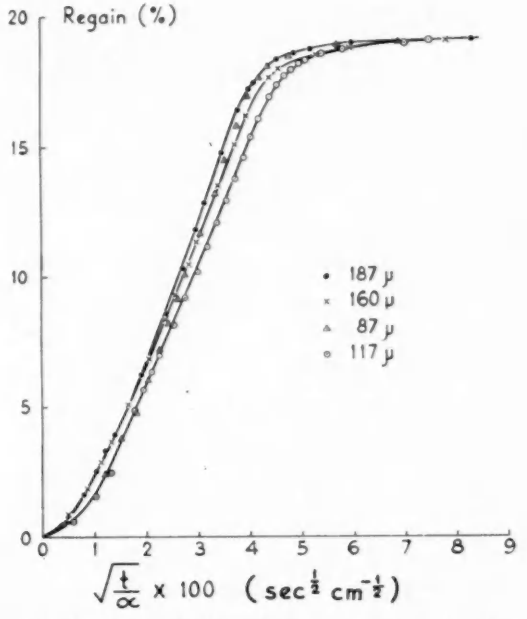

Fig. 11. Data of Figure 8 for horse hair replotted on the basis of a direct diameter dependence of the diffusion time.

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Effect of the Technique of Exposure on the Characteristic Parameters which can be Derived from X-Ray Exposures of Rayon[1]

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Abstract

Attention is drawn to the distortion of the X-ray diffraction picture by "white radiation" when using a nickel filter and by radiation scattered by air. Means are proposed to minimize these effects. A new parameter is introduced to characterize the lateral order in rayons.

Introduction

Several attempts have been proposed to derive certain parameters from x-ray exposures of rayon fiber to characterize the fiber in question in relation to practical or research problems.

For routine investigations it is usual to employ nickel filtered copper radiation to produce the diffraction picture, with detection either by a photographic film technique followed by photometration or by use of a Geiger counter device. The use of monochromatized radiation is impractical in many laboratories, as it requires very long exposure times or too elaborate and costly apparatus.

Though distortion of the diffraction picture by the non-monochromatic components of the rays ("white radiation") when using a nickel filter is well known, it seems that many workers are not always well aware of its effects on the diffraction

[1] Communication No. 109.

TABLE I. Exposure Conditions Employed

No.	Camera	Radiation	KV	mA	Medium	Exposure time, min.
1	Astbury	Ni-filtered	20	140	Air	60
2	Astbury	Ni-filtered	40	100	Air	10
3	Astbury	Ni-filtered	20	27	Vacuum	120
4	Astbury	Monochrom.	40	120	Vacuum	120
5	Guinier	Monochrom.	40	100	Air	10
6	Guinier	Monochrom.	40	21	Vacuum	30

picture, nor of the effect of radiation scattered by air, which also contributes to the distortion.

This paper is meant to draw attention to these effects, illustrating the magnitude and nature of the errors and indicating to what extent they can be minimized.

Influence of Tube Voltage and Air Scattering

The effects in question can be best illustrated by showing equatorial photometer traces of exposures of one and the same arbitrarily chosen common textile rayon as taken with an ordinary Astbury fiber camera (flat film) and with a Guinier type (focusing bend crystal) camera (circular film) as described by De Wolff [2].

In Table I six different conditions of exposure used are specified.

Some exposures were taken with a high-power rotating anode tube (high amperage) and others with an ordinary Philips "Metallic" tube. In three cases the camera was evacuated to eliminate air scattering.

In Figure 1 the equatorial photometer traces of the exposures in the Astbury camera are shown and in Figure 2, those in the Guinier camera (which gives higher resolution; the effect of the divergence of the primary beam is practically negligible). In the Astbury camera the opening angle of the beam was 0°5′.

In all photometer scans a background line separating the crystalline diffraction from the diffuse background is tentatively drawn. In this regard we were guided by a special study on the background in cellulose diagrams (to be published separately).

The monochromatic exposure *in vacuo* (No. 4) should represent the true picture, free from contributions of parasitary radiation. By a procedure of normalization to equal height of the second maximum and subtraction, the contribution of parasitary radiation to No. 1, 2, and 3 is found, as indicated in the figures by the hatched areas.

In comparing No. 1 and No. 2 with No. 4, it is seen that considerable improvement in distortion can be obtained by reducing the tube tension from 40 KV to 20 KV. The voltage on which the tube is operated determines the proportion and composition of white radiation passing through the nickel filter as well as the total output of radiation. Both the proportion of white radiation and the output decrease sharply with decreasing tension.

By comparison of No. 1 and No. 3, both taken at 20 KV, it can be seen that the parasitary component in both is mainly white radiation. The exposure time at 20 KV had to be increased sixfold as

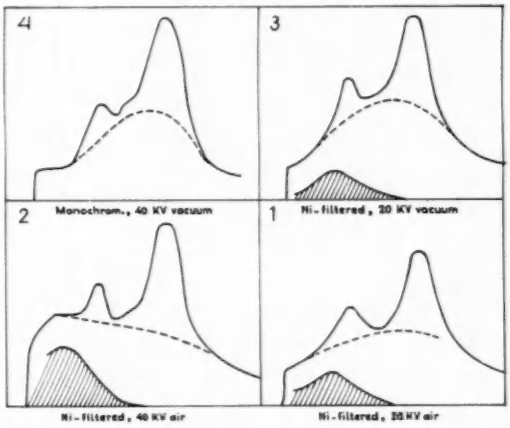

Fig. 1. Equatorial intensity distribution in x-ray exposures of a textile rayon with the Astbury camera at various conditions of exposure.

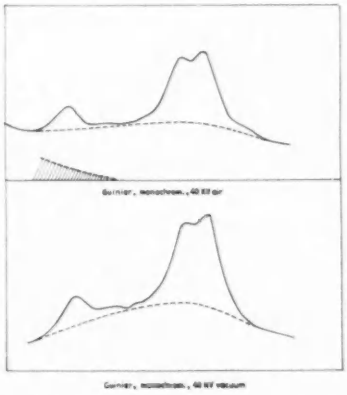

Fig. 2. Exposures of same specimen in focusing bend crystal Guinier camera.

TABLE II. Orientation Parameters

No.	Exposure	$\sin^2 \alpha_0$	$\sin^2 \alpha_2$	f_x
1	20 KV air (Ni)	0.058	0.147	0.69^3
2	40 KV air (Ni)	0.052	0.146	0.70^3
3	20 KV vac. (Ni)	0.052	0.149	0.69^3
4	40 KV vac. (mon.)	0.057^5	0.143	0.69^8

TABLE III. Values Normalized for Total Height in mm. of A_2 Peak = 100 mm.

No.	Exposure	A_0 peak	A_2 peak	Minimum
1	20 KV air Ni	17.2	56.5	47.5
2	40 KV air Ni	17.1	57	43
3	20 KV vac. Ni	17.9	55.5	50.5
4	40 KV vac. (mon.)	15.1	58	43.5
5	air (mon.)	16.9	57.5	43.8
6	vac. (mon.)	15.9	60:2	42.5

TABLE IV. *LO*-values According to Ingersoll's (I) and Our Own (II) Definition

No.	Technique	*LO* I	*LO* II
1	20 KV air (Ni)	22.6	26.5
2	40 KV air (Ni)	30.7	28.4
3	20 KV vac. (Ni)	17.2	26.1
4	40 KV vac. (mon.)	11.6	25.7
5	Guinier air (mon.)	28.4	27.8
6	Guinier vac. (mon.)	16.8	27.2

compared to 40 KV, but this sacrifice is rewarded by a much less distorted picture.

The two Guinier-camera exposures are shown in Figure 2. Owing to much better resolution, the A_2 and A_4 peaks, which overlap in Figure 1, are now separated. The contribution of air scattering in No. 5 is indicated by the hatched area.

The relative contribution of air-scattering is, of course, higher as the irradiated specimen layer is thinner. (Preferably, an effective layer thickness not less than 0.8 mm. should be used in practice if it is desired to keep air scattering low.)

It is important to note that even under the most unfavorable conditions (No. 2 in Figure 1) the parasitary radiation does not contribute beyond an angle of diffraction $2\theta = 16°$.

Orientation Parameters

In measurements of orientation according to the procedure developed in this and other laboratories [3], one is concerned only with readings of the relative heights of the peaks above the background line as a function of azimuth. This procedure has been applied in all four exposures shown in Figure 1, resulting in the figures listed in Table II.

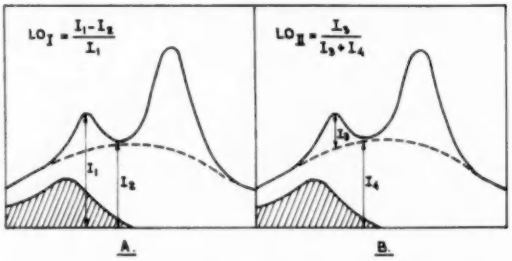

Fig. 3. Lateral order according to the definitions of Ingersoll (A) and the present authors (B).

It is seen that the orientation parameters are only insignificantly, if at all, affected by the exposure technique. The orientation factor f_x is practically the same in all cases. Fortunately, the orientation parameters are also insensitive to the way in which the background line is drawn.

For practical application it is recommended to draw the background line in the commonly accepted way with its maximum located at the minimum between A_0 and A_2 (as in Figure 3), irrespective of the fact that this is not quite correct.

If we normalize all the exposures of Figure 1 and Figure 2 to the total height of the A_2 peak = 100 (this is possible since no parasitary radiation takes part at this angle of diffraction) we can compare the measured heights of the peaks and that of the minimum between the peaks on all photographs. The result is given in Table III.

To include the Guinier exposures in the normalization, another correction is required. In order to make relative intensities measured on a cylindrical film at an angle of 2θ comparable with those taken on a flat film at that angle, the latter have to be divided by $\cos^2 2\theta$. This has been accounted for in Table III.

It is seen that the peak heights above the background are practically unaffected by the conditions of exposure. Contrarily, the minimum is affected, since there is still a contribution of parasitary radiation at the corresponding angle of diffraction.

Lateral Order

Ingersoll [4] has introduced a parameter named "lateral order" which also plays a significant role in the Cox patents of the DuPont Company and was proposed as a criterion for rayons with a special character [1].

This parameter is defined by Ingersoll as follows:

$$LO = 100\frac{L_1 - L_2}{L_1} \qquad (I)$$

where L_1 = total height of A_0 above zero line and L_2 = height of minima between the A_0 and A_3 peaks above the zero line; compare Figure 3A.

It follows from the foregoing that this parameter is greatly affected by the technique of exposure and *that it can be correctly determined only in monochromatic exposures carried out with an evacuated camera.*

We are now in the position to propose another similar parameter:

$$(LO) = 100\frac{L_3}{L_3 + L_4} \qquad (II)$$

where L_3 = height of A_0 peak above the *background* ($L_4 = L_2$ of the previous definition); compare Figure 3B.

This parameter, though still not quite independent of exposure technique, is very significantly less sensitive to it, since L_3 is free from the effects of parasitary radiation and L_4 only affected by a small proportion of it (see Figure 3B). This is illustrated by Table IV, where both parameters are tabulated for the six exposures from Figures 1 and 2.

It is seen that LO after the new definition is almost independent of the exposure conditions whereas *that after Ingersoll shows huge variations which invalidate any value of the parameter unless the x-ray picture is taken in vacuum and with strictly monochromatized radiation.*

Acknowledgment

The x-ray work was carried out by one of us (W) in the Physical Laboratory of the Technical University Delft.

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Polymerization and Condensation Reaction of N-Methylol Acrylamide within Cotton Fabric

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Abstract

Problems on the polymerization and condensation reaction of N-methylolacrylamide within cotton fabrics in which $K_2S_2O_8$, $(NH_4)_2S_2O_8$, or H_2O_2 was used as initiator and NH_4Cl or $(NH_4)_2HPO_4$ used as the acid condensation catalyst were investigated primarily from the standpoint of the crease resistance of the treated fabric. The results obtained are as follows.

The pre-drying process can be neglected, as almost the same result could be obtained even in the case of direct curing procedure, in which care should be taken not to over-cure.

Crease recovery and abrasion resistance (flat) of the treated fabric increased with higher value of resin content; tear strength, on the contrary, decreased presumably with some intrinsic cause.

The effect of the addition of acid catalysts such as NH_4Cl on the extent of the crease resistance was considerable, although some marked improvement was obtained in neutral catalysts such as $K_2S_2O_8$ alone.

The addition of comonomers such as acrylamide and hexamethylene diamine HCl-salt as well as softeners to the treating bath was effective in improving the strength losses induced by this treatment. Aftertreatment of the N-methylolacrylamide-treated fabric with hexamethylenediamine or thereafter with formalin was also effective, since somewhat continuous distribution of the different kinds of network-structures within the fiber could be obtained by this procedure.

Durability of the treated fabric for boiling-alkali launderings was excellent.

Introduction

Many years have passed since attempts to deposit vinyl resins within cellulosic fibers such as cotton and viscose staple were initiated [4]. However, it is only in recent years that papers reporting the improvement of crease resistance by such procedures have appeared in the literature [2]. Geiger reported that methylol vinyl ketone, α-methylol vinyl ketone, and methylol vinyl ketone mixed with styrene could improve the crease resistance of fabrics by their effective inner depositions, followed by heat treatment, which causes cross-linking of the polymer molecule with the —OH group of cellulose.

We have investigated the properties of N-methylolacrylamide as a polymer source for several years and have found that this monomer has an interesting characteristic, inducing both polymerization and condensation reactions; the resultant polymer has a three-dimensional property the extent of which is optional [3]. Therefore, if this monomer were used for resin finishing of cellulosic fabrics, it might be expected to impart a marked improvement of crease resistance without serious loss of strength.

This paper describes the observed results of the polymerization and condensation reactions of N-methylolacrylamide within cotton fabric and discusses the effect on such physical properties as crease resistance, tear strength, and abrasion resistance of the treated fabric.

Experimental

Materials

N-methylolacrylamide (CH_2=CH·CONH·CH_2-OH; MAM), acrylamide (35.5 g., 0.5 mole) and paraformaldehyde (15.0 g., 0.5 mole) were dissolved in 30 ml. of methanol with 0.3 g. of potassium hydroxide added and were then allowed to stand for 1 hr. at room temperature. The reaction mixture which formed during this time and from which the greater part of methanol was removed by evaporation under reduced pressure (10–20 mm. Hg) was dissolved in warm ethyl acetate and the resultant pre-

cipitate filtered off. The filtered solution was cooled to − 70° C. to yield crude crystals.

The crude product was recrystallized twice by dissolving it in warm ethylene chloride : ethyl acetate (2 : 1) and by cooling it below 0° C. A 70% yield was obtained, m.p. 72° C. (Lit. 74–5° C.).

The percent nitrogen calculated for $C_4H_7O_2N$ was 13.9; 13.7 was found. The amount of methylol group found by the iodometric method was satisfactory; free HCHO in aqueous solution was not found.

The cotton (40's) was desized and scoured.

Procedure

Aqueous solutions containing MAM, reagent grade peroxide catalysts ($K_2S_2O_8$, $(NH_4)_2S_2O_8$, H_2O_2, etc.), and acid ones (NH_4Cl, $(NH_4)_2HPO_4$, etc.) were made up to a specified volume. After being thoroughly impregnated with the solution, cotton was padded, dried, cured, and scoured by the usual procedure; thereafter N content was determined by the Kjeldahl procedure.

Testing Methods

All tests were carried out at 20° C. and 65% RH along the warp alone. Crease recovery was determined by the Monsanto wrinkle recovery tester. Tear strength by the Elmendorf's tester and abrasion resistance (flat) by the Custom Universal Wear Tester were also determined. With some samples, a rather severe laundering test in which they were boiled in an alkaline solution containing 0.5% soap and 0.2% soda ash for 1 hr. was done.

Results and Discussion

Stability of Aqueous N-Methylolacrylamide Solution Under Acidic Conditions

The stability of MAM monomer in the treating bath is a problem not to be ignored from a practical standpoint. It was reported that MAM gave N,N'-methylenebisacrylamide under acidic conditions using ethylene chloride as the reaction medium.

$$2CH_2{=}CH{\cdot}CONH{\cdot}CH_2OH \xrightarrow{\text{acid}} (CH_2{=}CH{\cdot}CONH)_2CH_2 + HCHO + H_2O \quad (1)$$

In aqueous solution, however, MAM is extremely stable, as shown in Figure 1, in which the —CH_2OH concentration was determined by the usual iodometric method. These results probably may mean that some HCHO- or H_2O-liberating conditions such as solid state are required to induce the reaction described above.

Effect of Pre-Drying Conditions

As is illustrated in Figures 2 and 3, the pre-drying process does not affect the results; the values of the crease recovery and the Elmendorf tear strength of the cured fabric did not greatly vary with the time and temperature of pre-drying, while in the dried sample (uncured) considerable change in the amount of the deposited resin as well as the value of the crease recovery can be observed.

Effect of Curing Conditions

The effect of the curing temperature and time on the extent of resin formation and on the mechanical

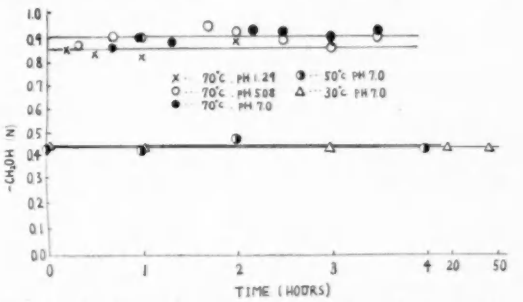


Fig. 1. Stability of aqueous N-methylolacrylamine solution under acidic conditions.

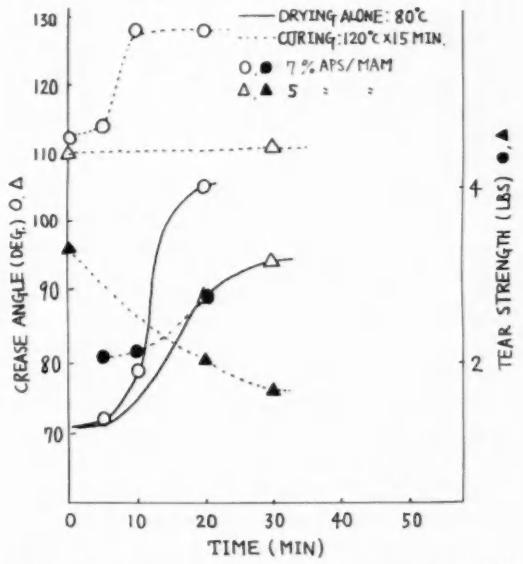


Fig. 2. Effect of pre-drying time (monomer add-on, 12%).

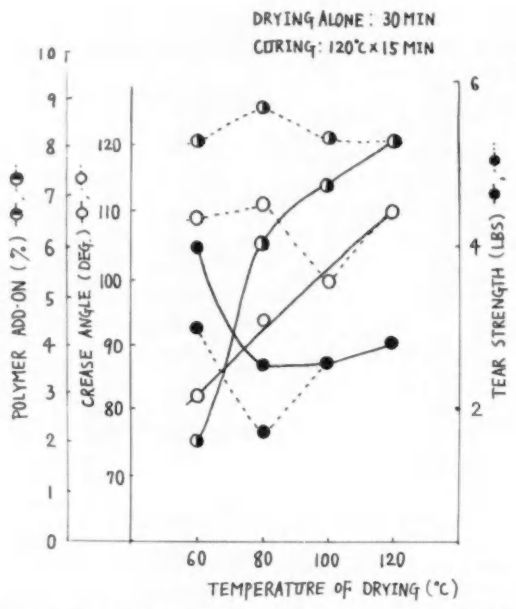


Fig. 3. Effect of temperature of drying. 5% $(NH_4)_2S_2O_8$ (APS) was used as the polymerization and condensation catalyst; polymer add-on in each case was 12%.

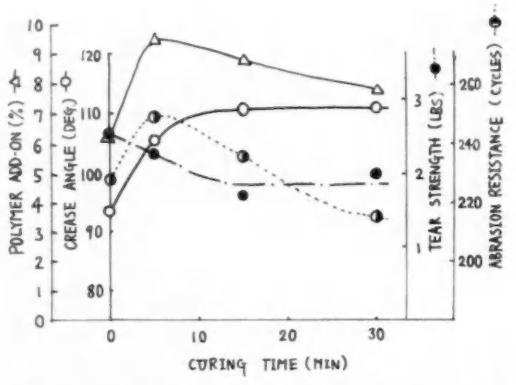


Fig. 4. Effect of curing time. All samples were dried for 30 min. at 80° C. and then cured at 120° C. Monomer add-on, 12%. 5% $(NH_4)_2S_2O_8$ monomer was used.

properties of the treated fabric were investigated.

It is apparent from Figure 4 that increasing the curing time up to about 5 min. resulted in higher values of the abrasion resistance, crease recovery, and resin content in the fabric. Abrasion resistance and resin content, however, decreased when the curing time exceeded this value.

A similar maximum is observed in Figure 5 about

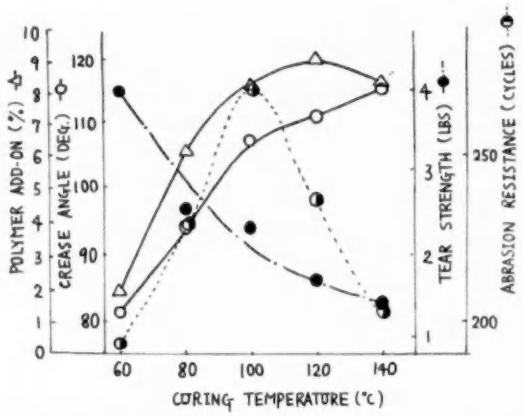


Fig. 5. Effect of curing temperature. All conditions were the same as in Figure 4, except that 15 min. was used as curing time.

100° C.; these peculiar phenomena might be attributed to the difference in the extent of cross-linking of the polymer produced within fibers.

The mechanism of the reaction which takes place in the fiber during these stages of the pre-drying and subsequent curing processes may be presented as follows.

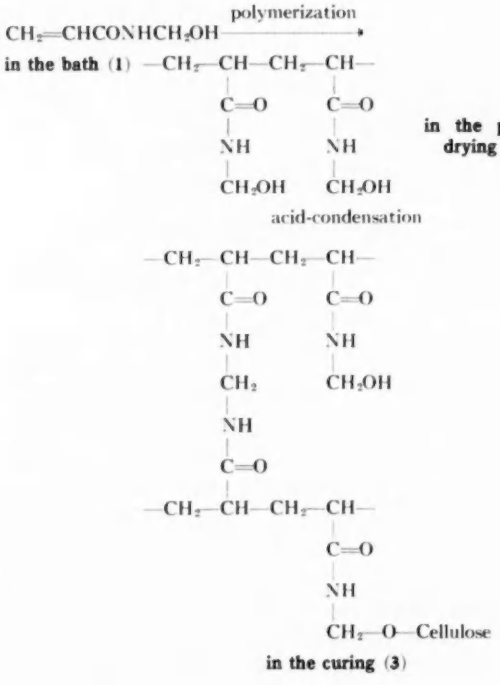


TABLE I. Use of Organic Solvents as the Bath Medium*

Solvent		Crease angle, deg.	Tear strength, lb.	Abrasion resistance, cycles
Dimethyl-formamide	uncured	72	4.58	197
	cured	127	2.32	206
Dioxane	uncured	72	3.78	160
	cured	144	1.72	251
Isopropyl alcohol	uncured	72	4.20	173
	cured	137	2.04	174
Acetone	uncured	75	4.96	179
	cured	125	2.08	175
Untreated	—	71	5.76	184

* All experiments were carried out with 12% monomer add-on using 10% azobisisobutyronitrile and 5% hexamethylenediamine HCl-salt as the catalyst. Drying: 80° C., 30 min. Curing: 120° C., 15 min.

The main part of the formation of polymer with three-dimensional characteristics seems to be due to this reaction mechanism, although the occurrence of the cross-linking reaction at the (2) stage as well as the polymerization reaction in the (3) stage is expected to some extent. From this supposed mechanism of the polymer formation, it is very likely that the network structures thus formed are somewhat weaker in three-dimensional properties than those of usual condensation-type resins such as urea-formaldehyde, melamine-formaldehyde, etc. Accordingly, at the optimum extent of cross-linking (i.e., at the most proper temperature and time of the curing process) the polymer produced is most elastic and tenacious, simultaneously improving both crease resistance and strength of the treated fabric. When the extent of cross-linking exceeds this optimum range, however, the polymer becomes more brittle and harder, causing loss of the surface polymer through scouring and thus leading to a decrease in abrasion resistance, as is the case in usual thermosetting resins.

Use of Organic Solvent as the Bath Medium

In usual resin-finishing procedures, the problem of the permeation of resin monomer into the fiber is of importance. Therefore, several organic solvents of MAM were used here as the impregnating bath to examine the effect of the surface polymer on the mechanical properties of the treated fabric (Table I).

The results obtained indicate that all of the organic solvents used can improve the crease recovery to the same extent as water.

Among others, it should be noted that even isopropyl alcohol and acetone can markedly improve crease resistance, although they are considered as rather poor in permeating the fiber. This fact, together with the fact that the pre-drying process is almost unnecessary, leads to some unique characteristic of the resin finish with this polymerization and condensation type monomer, in which even polymer deposited in comparatively outer parts of the microscopic structure of the fiber is considered to improve, or at least not to lower, the crease resistance of cellulosic fabrics such as cotton.

TABLE II. Effect of the Kind of Polymerization and Condensation Catalyst*

Catalyst	Crease recovery, %	Tear strength, lb.	Abrasion resistance, cycles
Untreated	39	5.76	184
5% $(NH_4)_2S_2O_8$	61	1.76	236
5% $K_2S_2O_8$	65	2.20	170
5% $K_2S_2O_8$+5% ammonium chloride	75	1.66	185
10% $K_2S_2O_8$+5% ammonium chloride	79	1.56	139
5% H_2O_2	46	3.28	145
5% H_2O_2+5% ammonium chloride	73	1.92	153
10% H_2O_2+5% ammonium chloride	71	2.08	204

* All experiments were carried out with 12% monomer add-on. The fabric was pre-dried for 30 min. at 80° C. and then cured for 15 min. at 120° C.

TABLE III. Effect of Polymerization Catalysts upon Strengths of Cotton Fabric

Catalyst	Tensile strength, kg./cm.	Tear strength, Elmendorf units
Untreated	8.27	5.46
1.2% Azobisisobutyronitrile	9.07	4.58
0.6% $K_2S_2O_8$	4.47	2.16
0.6% $(NH_4)_2S_2O_8$	5.93	3.30
0.6% H_2O_2	8.58	4.86

Effect of the Kind of Catalyst

The effect of the polymerization and condensation catalyst under typical conditions is seen in Table II.

The most striking difference in this table is found in the values of crease recovery of samples using

$(NH_4)_2S_2O_8$, $K_2S_2O_8$, or H_2O_2 as the polymerization catalyst together with NH_4Cl as the acid-condensation catalyst and those using the former alone. It is confirmed from this that the effect of the acid catalyst on the extent of the cross-linking reaction between the polymer chain and cellulose molecule and in the polymer itself is so large as to necessitate its use.

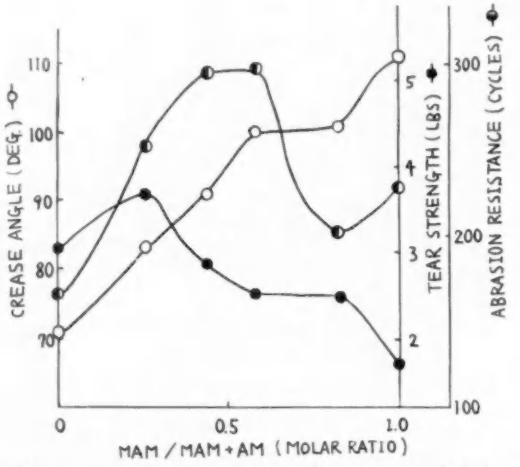


Fig. 6. Effect of the addition of acrylamide (AM) to the treating bath. Total monomer add-ons were 12%; 5% APS was used as the catalyst. The fabric was predried for 30 min. at 80° C. and then cured for 15 min. at 120° C.

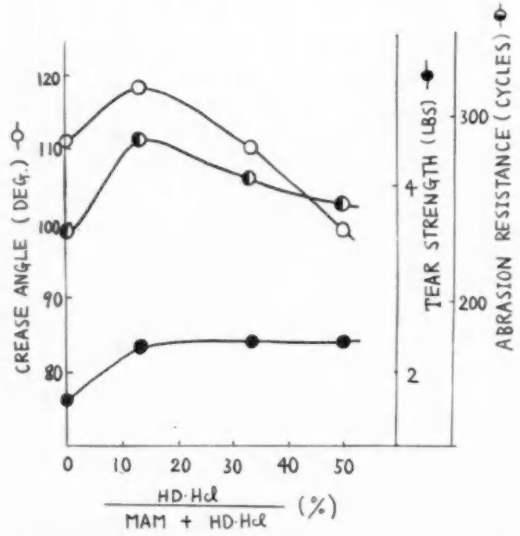


Fig. 7. Effect of the addition of hexamethylenediamine HCl salt (HD·HCl) to the treating bath. All conditions were the same as in Figure 6.

It is also noteworthy that some pronounced effect was obtained even with neutral peroxide catalysts (especially $K_2S_2O_8$) alone, which is supposed to be due to the formation of the network structure of MAM polymer through cross-linking reaction by radical mechanisms [3]. However, the differences among the effects of these catalysts upon strengths is not clearly discernible in this table. The strength loss of the cotton fabric treated with polymerization catalyst alone is shown in Table III.

It is found that the fabric treated with $K_2S_2O_8$ or $(NH_4)_2S_2O_8$ suffers a marked decrease in tear and tensile strength, presumably due to the oxidative degradation of cotton cellulose. H_2O_2, different from these, scarcely affects cotton strength, since the oxidative action is supposed to be weaker in this catalyst and its larger part is given off at the predrying stage. It is also found that azobisisobutyronitrile does not affect the fabric at all since this catalyst possesses the radical-forming property alone and does not show any oxidative action. However, it is insoluble in water. Accordingly, it is recommended that H_2O_2 with an acid catalyst (e.g., NH_4Cl) should be used as the mixed catalysts for the polymerization and condensation reactions of MAM.

Use of Additives

It is well known that treatments of the surface of fibers with softeners are effective in reducing the strength damage produced by thermosetting resins. It has also been reported that the inner deposition of linear vinyl polymers to cellulosic fabrics produces improved abrasion resistance [5]. Therefore, in our study the following three methods were put into practice in order to reduce the strength damage resulting from the MAM treatment.

1. Acrylamide and hexamethylenediamine HCl-salt were added to the treating bath for participating in the polymerization and condensation reaction respectively for controlling the flexibility of the network structure produced.

2. Several soft resin emulsions and lower molecular weight softeners were also added to the bath.

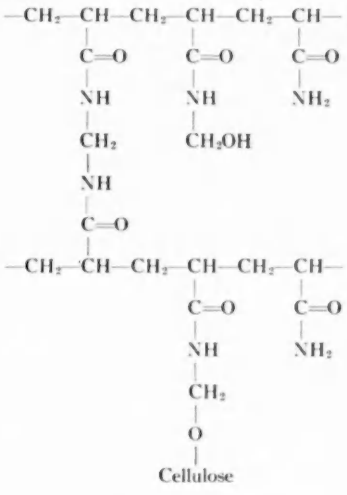
3. MAM-treated fabrics (uncured) were after-treated with hexamethylenediamine or with formaldehyde again. It is likely that this results in somewhat continuous distribution of the different kinds of the network structures of the polymer produced between the inner and outer part of the submicro-

scopic structure of the cotton fiber. As shown in Figure 6, the higher the ratio of acrylamide (AM) in monomer mixtures, the lower is the value of crease recovery; this relation is reversed in the case of Elmendorf's tear strength.

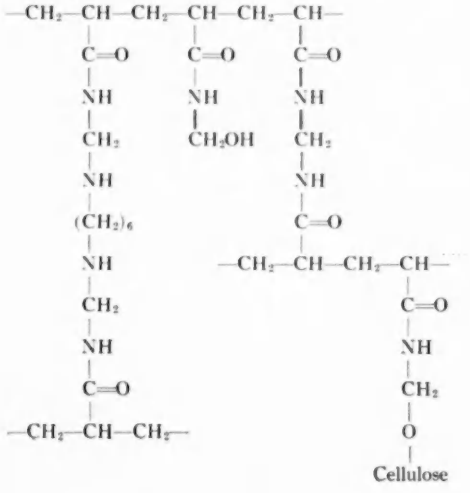
In the values of the Universal Abrasion Resistance, however, a maximum at about 0.6 molar ratio of MAM is observed; it can be interpreted as the optimum point representing a moderate degree of cross-linking. A similar maximum concerning crease recovery as well as abrasion resistance is also found in Figure 7.

The assumed network structures are shown below.

1. Acrylamide



2. Hexamethylenediamine



As shown in Figures 8, 9, and 10, with several softeners crease recovery enhancement accompanied by lowering of the tear strength decrease due to the MAM treatment is observed. Among them, octadecylethyleneurea was most effective in improving tear strength, yet it is rather poor in improving abrasion resistance, since homogeneous film formation on the surface of the fiber might be impeded by its intervention.

The third procedure, aftertreatment with hexamethylenediamine or thereafter with formalin, is the same in principle as adding hexamethylenediamine HCl-salt to the treating bath. However, the decrease of the power of hexamethylenediamine to permeate the submicroscopic structure of cellulose

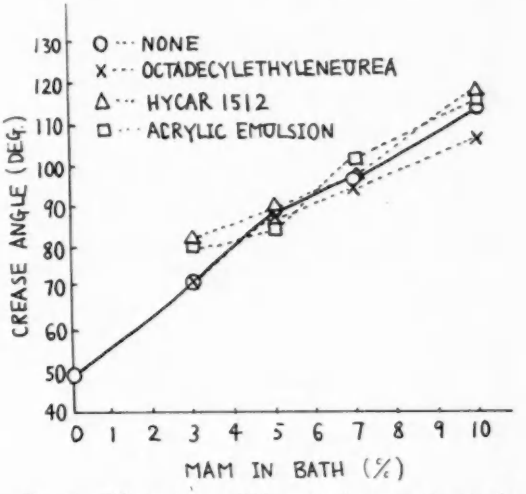


Fig. 8. Effect of the addition of softener to the treating bath (1). 1% H_2O_2 and 0.5% ammonium chloride were added to the treating bath as catalyst; 5% softener was also added. The fabric was cured for 20 min. at 110° C. without pre-drying.

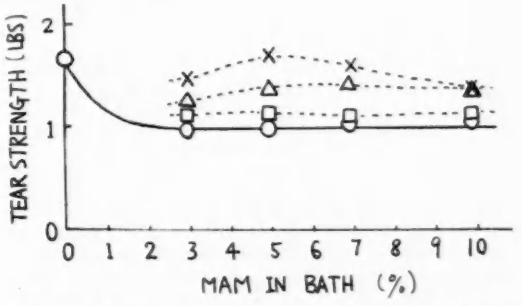


Fig. 9. Effect of the addition of softener to the treating bath (2). The applying conditions were the same as in Figure 8.

fiber once the MAM polymer was pre-deposited was utilized in this case. Accordingly, it is supposed that the network structure of polymer within fibers is more rigid and tenacious in the inner part, while it is more flexible and softer in the comparatively outer part. This apparently continuous distribution of the network structure perhaps leads to the improvement of crease resistance with all resins and to the moderation of the strength damage induced by the inner resin. Figure 11 shows these results. It should be noted that the hexamethylenediamine aftertreatment followed by impregnation with formalin is most effective in improving both crease and abrasion resistance, presumably due to the formation of a more complete network of polymer. Moreover, cellulosic fabrics thus aftertreated are readily dyed with acid dyes, so this procedure may be used for the dyeing of mixed cellulosic fabrics such as viscose staple–nylon with usual acid dyes and simultaneously for obtaining crease- and shrink-proofing effects.

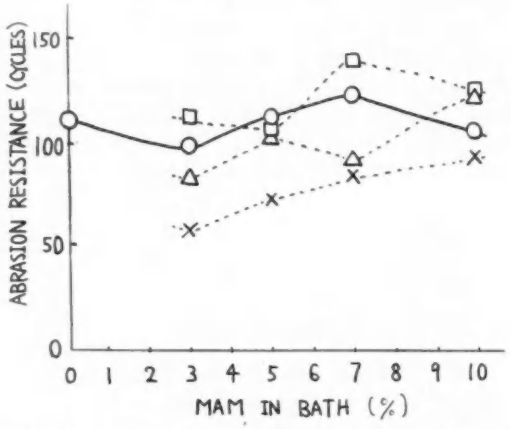


Fig. 10. Effect of the addition of softener to the treating bath (3). The applying conditions were the same as in Figures 8 and 9.

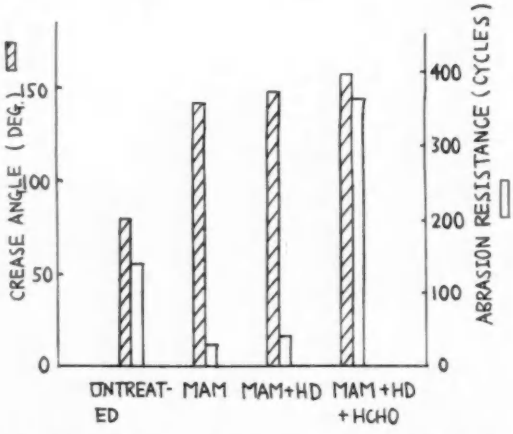


Fig. 11. Effect of aftertreatment in the MAM finish. (A) MAM: fabric was immersed in 20% aqueous MAM solution containing 1% APS and 2% $(NH_4)_2HPO_4$/MAM as catalyst, dried for 30 min. at 80° C., then cured for 5 min. at 150° C. (B) MAM + HD: fabric treated with MAM according as the above procedure, but uncured, dipped in 10% HD solution, dried for 30 min. at 80° C., then cured for 10 min. at 120° C. (C) MAM + HD + HCHO: the (MAM + HD) treated uncured fabric was immersed in 2% aqueous formalin, dried for 30 min. at 70° C., and cured for 10 min. at 120° C.

Effect of Laundering

An experiment was next designed to evaluate the effect of alkali-laundering; the procedure is described above. It is noteworthy that the fabric treated with MAM alone showed a marked resistance to such alkali-boiling launderings as compared with aftertreated samples (Table IV). This apparent behavior of MAM similar to that of the "reactant-type" resin might be due partly to the formation of cross links between —CH_2OH groups of the MAM-polymer and —OH groups of the cellulose molecule and partly to the excellent resistance of cross links produced between polymer chains to alkali decomposition, since under ordinary laundering conditions no visible change of crease resistance in any case in Table IV was recognized.

Correlation of Crease Recovery with Tear Strength

It has been generally accepted that the decrease of tear strength due to the increase of crease re-

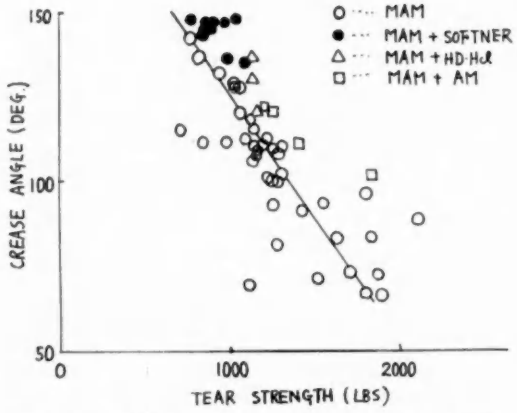


Fig. 12. Variation of tear strength with crease angle.

TABLE IV. Effect of Alkali Launderings

Treatment	Crease recovery, %		
	Original	After 1 wash	After 5 washes
Untreated	44.3	—	—
MAM alone	78.8	77.8	80.6
MAM + HD	82.3	65.1	59.4
MAM + HD + HCHO	87.3	66.7	64.0

sistance is inevitable in usual finishes with thermosetting resins [1]. Therefore, the value of crease recovery was plotted against Elmendorf's tear strength under various conditions, as shown in Figure 12.

Comparatively minor differences are found between the values of crease recovery at the same extent of tear strength and an almost linear relation can be obtained with MAM used alone. Accordingly this relationship might be attributed to some extent to a somewhat intrinsic cause, although it is also dependent upon such variables as texture, site of the deposited polymer, etc. The diagram further indicates that use of additives is effective in improving this relationship.

Summary and Conclusions

Crease resistance and, under proper conditions, abrasion resistance too were excellent in the cotton fabric in which MAM polymer was deposited. It has been also found that the application of MAM to the fabric was slightly affected by the temperature and the time of the pre-drying process and the medium of the treating bath. This might be due to the formation of rather weakly cross-linked polymer within fibers and to the occurrence of cross-linking reaction between the polymer and cellulose molecule. For the catalyst group most adequate to the polymerization and condensation reaction H_2O_2 added with NH_4Cl can be recommended. Use of additives in the bath was effective in reducing the damage induced by this treatment; aftertreatment with hexamethylenediamine or thereafter with formalin also gave excellent results.

Acknowledgments

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The True Index of Non-Uniformity for Jute Yarn

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Abstract

A theoretical expression for the non-uniformity of random jute yarn has been derived from the fineness–length relation and the distribution of length of the filaments in the yarn. The ratio of the actual measured non-uniformity of the yarn to this theoretical value has been suggested to be a true index of non-uniformity due to processing.

Introduction

The variation of mass per unit length or thickness along the length of sliver is not entirely the result of variation in processing; part of it is inherent in the sliver because of the gaps existing between the ends of consecutive fibers. An estimate of the contribution of this latter cause is needed for a proper evaluation of the effects of processing.

For this purpose Spencer-Smith and Todd [11] introduced the concept of an ideal sliver in which the fiber ends are displaced at random along its length. From theoretical considerations they arrived at an expression for the coefficient of variation of such an ideal sliver in which they idealized the fibers as of uniform cross section and accounted for cross-section variation between fibers in terms of a length function, because the cross section of flax fibers, with which they were working, was related to fiber length. The ratio of the measured coefficient of variation of the actual sliver to the coefficient of variation of the theoretical sliver was considered by them to be a basis of comparison of non-uniformity irrespective of the weight or the cross-sectional area of the fibers. This ratio was later [8] termed the "True Index of Irregularity."

Martindale [7] and Huberty [6], working on wool, obtained slightly different expressions. Picard [10] has shown that all these expressions are only special cases of a more general equation derived by him directly from a consideration of the variation in count (weight per unit length).

The object of the present work is to obtain an expression for the coefficient of non-uniformity of a random yarn of jute fiber and a True Index of Non-Uniformity and to compare their values for different types of jute. The treatment of Spencer-Smith and Todd is most suitable for this purpose, because the mass per unit length of the individual filaments of jute fiber as they occur in yarn has been found to be linearly related to filament length [2]. The irregularity within individual filaments has been neglected, although it may be considerable due to the complex and branchy nature of the filaments.

Theoretical

For the ideal sliver of Spencer-Smith and Todd [11] the CV % (C) of cross section was given by

$$\left(\frac{C}{100}\right)^2 = \frac{1}{\alpha} \cdot \frac{\int_0^{l_m} l \cdot f(l) \cdot [F(l)]^2 dl}{\int_0^{l_m} l \cdot f(l) \cdot [F(l)] dl} \tag{1}$$

where $f(l)$ denotes the frequency of a fiber group of length l, $F(l)$ represents the area of cross section of a fiber of length l, l_m the maximum length, and α the total area of all the fibers in a sliver section. In the light of Picard's deductions this relation may be used for mass variation as well, provided local counts or mass per unit length values over very short regions are considered. Then W, the mass per unit length of the sliver, will replace α, and $F(l)$ will represent mass per unit length of filament as a function of length.

For fiber filaments from jute yarn it has been found [2] that the length distribution function $f(l)$, on a number basis, is of the form

$$f(l) = Y_0 l^p e^{-al} \tag{3}$$

where Y_0, p, and a are constants, and

$$F(l) = m_0 + \Delta l \tag{4}$$

represents the fineness–length relation, where m_0 is the extrapolated value of mass per unit length for extremely short fibers and is called intrinsic fineness; Δ is the slope of the line.

If the twist is neglected, a yarn is equivalent to a

sliver. Hence the percentage coefficient of mass variation (V_r) of the ideal or random yarn is given by

$$\left(\frac{V_r}{100}\right) = \frac{1}{W}\cdot\frac{\int_0^{l_m} l\cdot l^p e^{-al} m_0^2 \left(1+\frac{\Delta}{m_0}\cdot l\right)^2 dl}{\int_0^{l_m} l\cdot l^p e^{-al} m_0 \left(1+\frac{\Delta}{m_0}\cdot l\right) dl} \qquad (5)$$

Using infinity for the maximum length l_m, and integrating with the help of gamma functions, one may reduce the expression to

$$\left(\frac{V_r}{100}\right)^2 = \frac{m_0}{W}\cdot\left[1+\frac{\Delta}{m_0}\cdot\frac{p+2}{a}+\frac{\left(\frac{\Delta}{m_0}\right)^2\cdot\frac{p+2}{a^2}}{1+\frac{\Delta}{m_0}\cdot\frac{p+2}{a}}\right]$$

If $\bar{l}$ and ϑ are the average and (fractional CV)^2 of filament length, then, by substitution of β for $(\Delta/m_0)\cdot\bar{l}$ the equation for V_r takes the form

$$\left(\frac{V_r}{100}\right)^2 = \frac{m_0}{W}\cdot\left[1+\beta(1+\vartheta)+\frac{\beta^2\vartheta(1+\vartheta)}{1+\beta(1+\vartheta)}\right]$$
$$= \frac{m_0}{W}\cdot\phi \qquad (6)$$

ϕ is substituted for the terms within the square bracket.

If in Equation 1 the integrations are replaced by summations; $f(l)$ by n, the number of filaments in a length group (l); and $F(l)$ by m_l, the average fineness for that group, we get

$$\left(\frac{V_r}{100}\right)^2 = \frac{1}{W}\cdot\frac{\Sigma l\cdot n\cdot m_l^2}{\Sigma l\cdot n\cdot m_l}$$
$$= \frac{1}{W}\cdot\frac{\Sigma w\cdot m_l}{\Sigma w}$$

where w is the weight of a particular length group. Then $\Sigma w\cdot m_l/\Sigma w$ is simply the weight-average of filament fineness, represented by m_w. Hence

$$\left(\frac{V_r}{100}\right)^2 = \frac{m_w}{W} \qquad (7)$$

When the fiber has been processed and we have it in the form of a sliver or yarn it is easier to obtain m_w instead of $m_0\phi$. The latter form is, however, suitable when it becomes necessary to predict V_r from the properties of unprocessed raw jute.

If V be the measured CV% of actual yarn the True Index of Non-Uniformity will be

$$I_T = \frac{V}{V_r} = V\cdot\sqrt{\frac{W}{m_0\phi}} \quad \text{or} \quad V\sqrt{\frac{W}{m_w}} \qquad (8)$$

in which the contribution toward yarn irregularity of the variations in yarn and fiber counts has been fairly accounted for.

Experimental

The methods of determining m_w and m_0, and other length parameters, are reported elsewhere [2]. The yarn count W was obtained in the usual way. The actual irregularity (V) of the yarn was measured on a Uster Evenness Tester [1] Model B at normal setting; that is, with equivalent test length of 8 mm., which is quite small for jute yarns. The capacitance variation of the evenness tester was taken as a faithful representation of mass variation. When comparing different varieties of jute, 10-lb. hessian weft yarns were produced under standard [9] conditions.

Results and Discussion

Table I gives the values of mass per unit length W and the measured coefficient of variation V of several standard yarns spun from jute fibers of a wide range of quality. The table also gives the values of m_w, m_0, and ϕ, calculated from the fineness and length characters of the filaments of these yarns obtained from the results of analysis reported elsewhere [2]. The coefficient of variation V_r of random yarn and the True Index of Non-Uniformity I_T have been calculated and given in the table.

It will be seen that, on an average, while V is 33%, V_r is only 10%. The variation of V_r from sample to sample is also within a small range of 9–12%. Thus the minimum variance V_r^2 accounts for only a tenth of the total variance V^2. The major part of the variance is, therefore, due to processing factors.

The results of 19 yarns indicate that the range of variation of I_T is 1:1.8, which is somewhat wider than that of V; this is advantageous for comparative work. Moreover, the ranking of the samples on the two scales does not always agree; in about 25% of the cases the disagreement is by wide margins. The V-scale indicates, as it should, that the yarn made from finer fiber (No. 1) is more regular than that from a coarser fiber (No. 16), while on the I_T-scale the order is reversed and the values differ widely. A consideration of the effects of fiber association [4, 5, 8, 12] and filament length [4, 5] will however, explain this.

The consideration of the True Index of Non-Uni-

TABLE I. Yarn Characters, Filament Properties, and the True Index of Irregularity of Different Types of Jute

Sr. No.	Yarn characters: Count, W, tex	Yarn characters: Uster CV, V,%	Filament properties: Fineness, tex: m_w	Filament properties: Fineness, tex: m_0	Filament properties: ϕ	Filament properties: $m_0\phi$	Random CV, V_r,%	True index (I_T), $\frac{V}{V_r}$
1	403	29.3	2.41	1.10	2.25	2.48	7.9	3.7
2	379	28.3	3.01	1.60	1.89	3.02	8.9	3.2
3	389	32.5	3.04	1.00	3.69	3.68	9.7	3.4
4	355	31.5	3.07	1.50	2.24	3.36	9.7	3.2
5	407	34.1	4.09	2.00	2.07	4.14	10.1	3.4
6	417	36.1	4.83	2.60	1.96	5.10	11.1	3.3
7	365	33.1	3.15	1.90	1.57	3.08	9.0	3.7
8	351	31.7	3.03	1.80	1.63	2.93	9.1	3.5
9	358	33.7	3.47	1.92	1.65	3.17	9.4	3.6
10	358	36.9	3.82	1.70	2.06	3.50	9.9	3.7
11	345	34.8	3.47	1.84	1.89	3.48	10.0	3.5
12	372	32.7	3.53	1.94	1.64	3.18	9.3	3.5
13	348	29.6	3.49	2.00	1.80	3.60	10.2	2.9
14	331	33.1	3.45	1.95	1.84	3.59	10.4	3.2
15	348	28.3	4.42	2.50	1.76	4.40	11.2	2.5
16	348	31.7	5.10	2.30	2.20	5.06	12.1	2.6
17	393	36.1	4.47	2.60	1.71	4.45	10.6	3.4
18	345	32.7	3.45	1.80	1.94	3.49	11.7	2.8
19	314	43.9	2.77	1.43	1.92	2.75	9.4	4.6

formity is, therefore, of great importance in analyzing the causes of irregularity, for it reveals the true effects of processing. But its use will be limited if V_r has to be calculated after length analysis. Its prediction from the original fiber characters may, however, improve its usefulness. As a matter of fact, it has been possible to predict [2] m_0, but not the quantity ϕ, from m_c, the fiber fineness value after exhaustive combing of raw fiber and cutting to very small lengths. When comparing yarns, since ϕ normally varies within small limits, for practical purposes it may be taken as constant and equal to its average value, 2.0 approximately; I_T will then be equal to a constant $\times V\sqrt{W}/\sqrt{m_c}$).

When comparing yarns of different counts spun from the same fiber, m_c being constant, one may use the equation

$$I = \text{const.} \times V\sqrt{W} \qquad (9)$$

as an Index of Non-Uniformity, as done by Banerjee and Sen [3]. But in comparing the irregularities of products at different stages of jute yarn manufacture, I_T (Equation 8) would be a better index than I, because during processing jute filaments are gradually split up and the value of m_w is reduced [2] by about 50% as the fiber passes from the card sliver to yarn stage. Moreover, "getting together" of filaments and the consequent increase of m_w has also to be considered.

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Length and Fineness of Jute Fiber Filaments at Various Stages of Yarn Production and in Yarns of Different Qualities of Fiber

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Abstract

Changes in length and fineness of jute fiber filaments have been studied at different stages of yarn production, including carding, drawing, roving, and spinning. Length decreases and the filament becomes finer as processing progresses. The distribution of length and the length–fineness relation, however, remain similar in all stages. Filament length in yarns made by a standard process from different types of jute depends only slightly on fiber quality, while intrinsic filament fineness correlates fairly well with the filament fineness of unprocessed fiber.

Introduction

The importance of fiber length and fineness in determining the characteristics of spun yarn is well recognized [6, 9, 12]. Fiber breakage during yarn manufacture has, therefore, been studied in considerable detail in the case of other fibers. Little work has, however, been published on the dimensional characteristics of jute fibers during processing. This may be due to lack of a proper definition for the length and fineness of jute fiber, for, even after processing, the single entities into which the fiber is broken down retain some remnants of the meshy structure of jute in the form of branchings. For this work, however, such a single entity has been considered as one filament.

Reports on the dimensional properties of jute fiber filaments from yarn [4, 10], roving [2], and sliver [5] have been made. The object of the present work is to study the changes in length and fineness of jute fiber filaments as the same batch of fiber passes through the various processes involved in yarn manufacture and to find out how these characters are affected by the type of jute used.

Experimental

Yarn Manufacture

Long jute fibers were converted into 10-lb. hessian weft yarn by the standardized technique devised by Nodder and Gillies [7] and used in this laboratory for examining the spinning quality of agricultural samples. It consists essentially of two carding, two drawing, one roving, and one spinning process. Samples were taken from the following stages:

1. Sliver after first carding, referred to as breaker card sliver, weighing about 100 g./yd. (approx. 110 ktex).
2. Sliver after second carding, referred to as finisher card sliver, weighing about 80 g./yd. (approx. 90 ktex).
3. Sliver after second drawing, weighing about 24 g./yd. (approx. 27 ktex).
4. Roving of approx. 90 lb. grist (2.9 g./yd. or 3.1 ktex).
5. Yarn of 10 lb. grist (0.31 g./yd. or approx. 340 tex).

Measurement of Filament Length and Fineness

Sampling technique. The main difficulty in sampling was in drawing out one filament from a mass, for each filament may adhere to its fellows through its branchings. The disentanglement necessary for the purpose usually destroys the fiber arrangement. This has been guarded against by the following methods for obtaining representative samples.

For sliver and roving, 5-yd. lengths were cut from different zones, 5 for sliver and 8 for roving. Thin slices were then separated from these pieces by teasing them gently by hand, the roving being untwisted for the purpose. From each slice approximately 1 g. (0.6 g. for roving) of material was

broken off so that the total working sample was about 5 g. To break a slice it was held uniformly at two points, separated by a length greater than the longest possible filament, and drawn apart gently. The working sample was then further teased out and all the filaments were examined.

When examining yarns a working sample was drawn from 16 zones and consisted of only 0.5 g. of fiber having approximately 2000 filaments in all. The sampling technique adopted was a slightly modified form of Palmer's dye-sampling technique [8]. The line of demarcation between the dyed and undyed regions of the yarn was produced by compressing one portion of the material in a narrow rectangular slot by means of a plunger worked by a screw (Figure 1) and applying the dye solution on the projecting portion with a brush. Normally a 3-in. portion of each of 16 pieces of yarn (about 20 in. long) was dyed with methylene blue in this way. After the sample was dry, a band $\frac{1}{2}$ in. wide was dyed red with erythrosin on one side of the blue region; the yarn extending beyond the red region was cut as shown in Figure 2. The other side of the yarn sample was untwisted and broken, retaining the portion (A) which was always longer than the length of the longest filament. The filaments in this piece of yarn were then untwisted and teased out, and those with blue marks only were taken as the working sample. Such a sample contains all the filaments right (or left) ends of which fell within the 3-in. region of the yarn, prior to disturbing its fiber arrangement. Looped filaments were almost always absent. The sample is thus truly representative.

Determination of length and fineness. The distance between the two farthest tips of a filament was taken as the filament length; the length of the branches was not taken into consideration. The branches, however, contributed towards the weight of the filament. For slivers and untwisted rovings the filaments were measured in bunches by a process

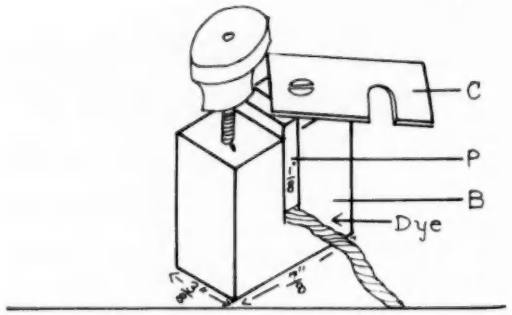

Fig. 1. Dyeing jig.

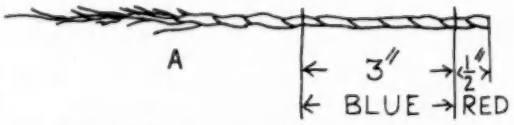

Fig. 2. Dye-sampling of filaments in yarn. Colored regions are shown.

of double drawing described earlier [2], while the filaments in the yarn were treated individually with two pairs of tweezers. A white scale on a black background was used. After the filaments were separated into different length groups, they were weighed on a sensitive balance. The percentage by weight of fibers in each group plotted against the average group length gave the length distribution curves. In the case of yarn, filaments were also counted and the percentages by number obtained. ASTM formulas [1] were used to calculate the average and the coefficient of variation of length on a weight basis (in the case of yarn, on a number basis also).

Fineness was determined by weighing on a sensitive balance portions of fiber taken from each length group and counting the number of separate filaments in each portion. The results were expressed in terms of weight per unit length (g./km. or tex).

Reproducibility of results. The reproducibility of

TABLE I. Comparison of Duplicate Determinations

Sample		Weight of sample, g.	Av. length by weight, in.	CV of length by wt., %
Breaker sliver (from 10 in cut reeds*)	I	5.0	6.39	43.3
	II	5.1	6.36	45.5
Roving (from full reeds)	I	4.5	6.02	53.6
	II	4.5	5.82	53.8

* A reed is a full length jute fiber.

the length-measuring techniques is illustrated in Tables I and II. Table II further shows how the effect of reducing sample size has been obviated by increasing the number of zones, so that the standard error of the mean value of length is maintained at a low level. The fineness value of a length group was the average of four determinations which did not usually vary beyond 10% of the mean.

Results and Discussions

Length

Variation from sliver to yarn stage. The frequency distributions of filament length by weight, at five different stages of yarn manufacture, were obtained for a medium quality jute (1) and a good quality jute (2) and were found to be single-humped and positively skew with a considerable bias towards shorter length at each stage. The values of length parameters, average, coefficient of variation, etc. are given in Table III. The average fiber length (10 in.) of low in card sliver gradually diminishes to half its value when the yarn stage is reached; the CV of length does not, however, change appreciably. The main causes seem to be the combing action of card pins and the closer and closer setting of feed and delivery rollers, which produces fiber breakage in successive stages. The distance between the rollers was 15 in. in the drawing, 11 in. in the roving, and 10 in. in the spinning frame. Each stage makes its own contribution to total breakage and splitting.

Variation with the quality of jute. Table III shows that the differences in the length parameters of different types of jute which may exist in the preliminary stages are largely reduced at the yarn stage. Even when fibers of widely different quali-

TABLE II. Effect of Sample Size Variation

Serial no. of experiments	No. of zones	Length of yarn taken from a zone, in.	Av. length of filament ± S.E., in.	Std. dev. of length, in.	CV of length, %	% of filaments above 6 in.	% of filaments above 7 in.
			By weight				
1	9	18	4.62 ± 0.044	2.35	50.8	27.4	16.8
2	3	18	4.83 ± 0.179	2.47	51.1	27.6	15.4
3	3	18	4.54 ± 0.156	2.09	45.9	23.4	11.8
4	15	3	4.54 ± 0.076	2.38	52.3	26.4	16.3
5	15	3	4.45 ± 0.088	2.33	52.4	24.4	16.5
			By number				
1	9	18	—	—	—	—	—
2	3	18	2.50 ± 0.096	2.00	81	6.8	3.6
3	3	18	2.51 ± 0.072	1.92	77	5.9	2.5
4	15	3	2.31 ± 0.077	1.94	84	5.6	3.1
5	15	3	2.32 ± 0.035	1.85	80	5.0	2.6

TABLE III. Length Parameters (by Weight) at Different Stages

Sample no.	Stage	Avg., in.	Std. dev., in.	CV, %	Max., in.	90% of fibers are below length, in.
Jute (1)	Breaker sliver	10.8	4.4	40.7	24	17
	Finisher sliver	7.8	3.8	48.5	24	13
	Roving	6.9	3.3	48.0	20	11
	Yarn	4.9	2.4	49.0	12	8
Jute (2)	Breaker sliver	9.4	5.9	62.4	32	18
	Finisher sliver	6.8	4.9	72.0	32	13
	2nd drawing sliver	6.2	3.8	62.0	20	12
	Roving	5.9	3.4	58.1	18	11
	Yarn	4.8	2.4	49.7	12	8

TABLE IV. Fineness in Tex of Individual Filaments (Including Adherents) at Different Stages

Stages	Weight-average fineness, m_w, tex		Intrinsic fineness, m_0, tex
	All groups	Groups 0–12 in.	
Breaker sliver	4.56	3.89	1.7
Finisher sliver	4.05	3.73	—
2nd Drawing sliver	3.65	3.46	1.7
Roving	3.23	3.08	1.6
Yarn	3.03	3.03	1.6

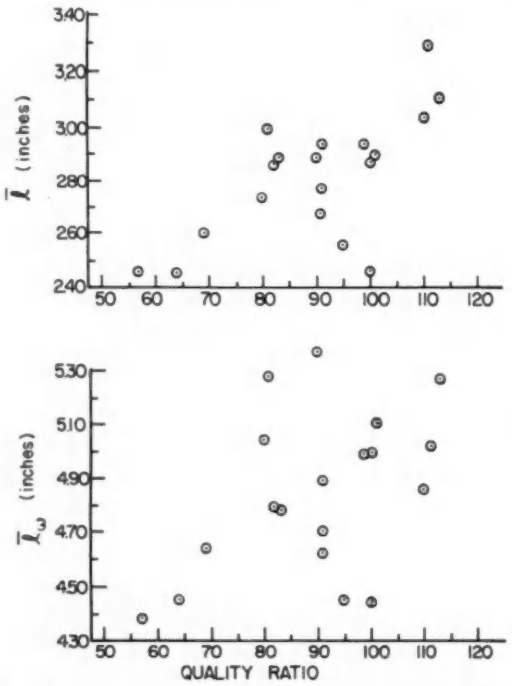

Fig. 3. Quality ratios of 10-lb. yarns and average lengths, $\bar{l}$ by number and $\bar{l}_w$ by weight, of filaments in yarns of different jute samples are correlated.

ties are considered (Table V), the variation among the average values of filament length in standard yarns spun from different fibers is small, but the difference between two averages is often significant. As a matter of fact, a higher value of average length tends to be associated with better fiber quality, as indicated by higher yarn quality ratio [100 × yarn strength (lb.)/weight (lb.) of 14,400 yd.]; see Figure 3. This view is supported by Figure 4, which shows how, within a sample, a longer filament (shorn of its branches) registers greater filament strength, measured at 1-cm. test length, as well as

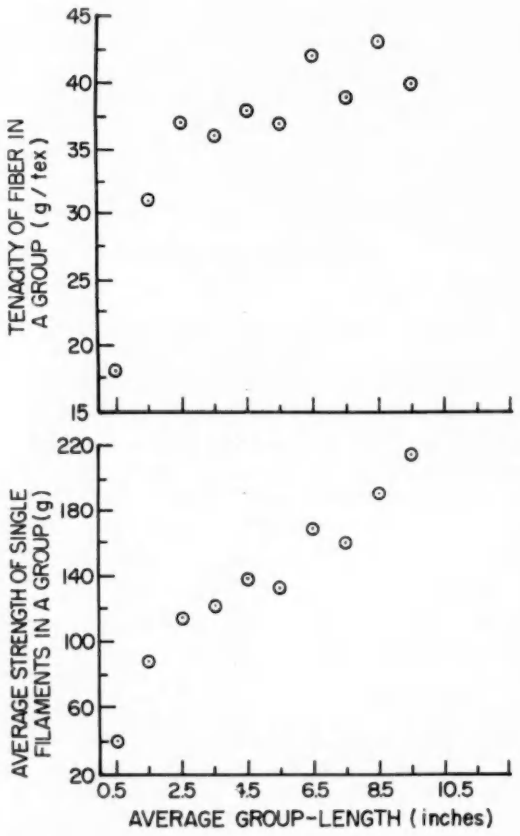

Fig. 4. Group-length in the length distribution of filaments in yarn is correlated with strength and tenacity of single filaments (shorn of branches).

higher tenacity. This explains that the longer filaments survive greater mechanical stresses during processing because of their higher strength.

Fineness

Variation from sliver to yarn stage. Table IV shows how the weight average of filament fineness (m_w), obtained by weighting the group-fineness values by the corresponding weights of fibers in respective length groups, is gradually reduced as processing proceeds from sliver to yarn. The first set of values, which includes all length groups, shows the joint effect of reduction in branching and of shortening the longer filaments which are usually more branchy. On the other hand, the second set, based on the groups lying between 0 and 12 in., which are common to all stages, suggests that the contribution of branch reduction is the major one.

Length–fineness curves. For each stage of processing, filament fineness has been plotted against group length; see Figure 5. It appears that at each stage the fineness or linear density (m_l) of a filament in a group is a function of group length (l). Leaving out the fibers longer than 12 in. which are too few in a group, the function may be expressed by the linear equation

$$m_l = m_0 + \Delta \cdot l \qquad (1)$$

where m_0 is the limiting value of fineness corresponding to the extrapolated value at zero length, hereafter referred to as intrinsic fineness, and Δ is the slope of the line.

From the method of measurement it is apparent that in any stage the increase in linear density (m_l) with length is due to an excess of branches or to some unbroken meshes in longer filaments. This view gets support in Table IV.

The slope Δ of the line is 0.34 tex/in. (0.14 tex/cm.) for the sliver stage, and gradually drops to 0.30 tex/in. (0.12 tex/cm.) for the yarn stage (Table IV). But the value of m_0, as obtained from the curves in Figure 5 and given in Table IV, does not alter appreciably during processing. It may be possible, therefore, to take m_0 as a parameter defining the intrinsic fineness of the fiber.

Variation with quality of jute. On examination of the filaments in yarns made from jute fibers of different qualities it was found that the fineness–length curve was essentially linear in each case, but the values of the intrinsic fineness m_0, as given in Table V, varied from 1.00 to 2.60 tex. Two other fineness parameters, the direct average ($\bar{m}$ = total weight/total length) and the weight average (m_w) are also given in the table for comparison, m_w being greater than $\bar{m}$. Of these the intrinsic fineness (m_0) will be found to be near the fineness values (m_c) of unprocessed raw jute obtained after a standard [3] exhaustive combing in one direction on fine gill pins over 2 cm. of a thin bundle; see Table V. Higher linear density of longer filaments must, therefore, be due to the existence of branches and unbroken meshes. Further, as shown in Figure 6, m_0 is fairly linearly corrlated with m_c, the coefficient of correlation being + 0.71. Thus m_0 can be obtained from m_c without processing the fiber. This justifies the definition of m_0 as an intrinsic fiber property.

Derivation of Length Distribution Function on Both Number and Weight Bases

Typical curves for filament length distribution in standard yarns, obtained on a number as well as a

TABLE V. Filament and Yarn Characters of Different Jute Fibers after Standard Processing

Serial no.	Yarn Q.R., $\left(\frac{100 \text{ lb.}}{\text{lb./spy.}}\right)$	Filaments from yarn: Length parameters, By weight: Av., l_w, in.	By weight: CV, %	By number: Av., $\bar{l}$, in.	By number: CV, %	Fineness parameters: Direct Av., $\bar{m}$, tex	Weight-Av., m_w, tex	Intrinsic m_0, tex	Δ tex/in.	Filaments from combed raw jute: Fineness, m_c, tex
1	100	4.44	51	2.45	74	2.22	2.41	1.10	0.31	1.58
2	91	4.62	48	2.76	71	2.87	3.01	1.60	0.30	1.97
3	64	4.45	48	2.45	74	2.66	3.04	1.00	0.57	1.54
4	99	4.99	46	2.93	72	2.93	3.07	1.50	0.36	2.14
5	80	5.04	49	2.73	80	3.77	4.09	2.00	0.41	2.30
6	57	4.38	52	2.46	76	4.56	4.83	2.60	0.55	2.78
7	111	5.01	44	3.28	65	2.97	3.15	1.90	0.21	1.83
8	110	4.85	47	3.03	68	2.88	3.03	1.80	0.23	2.04
9	100	4.99	50	2.86	75	3.16	3.47	1.92	0.25	1.96
10	91	4.70	50	2.67	75	3.31	3.82	1.70	0.37	1.69
11	83	4.78	50	2.88	74	3.26	3.47	1.84	0.32	1.72
12	82	4.79	50	2.86	71	3.23	3.53	1.94	0.26	
13	113	5.26	48	3.10	75	3.35	3.49	2.00	0.29	2.08
14	101	5.10	49	2.89	79	3.25	3.45	1.95	0.30	1.91
15	90	5.36	52	2.88	83	4.17	4.42	2.50	0.34	2.56
16	81	5.27	45	2.99	75	4.61	5.10	2.30	0.50	2.60
17	69	4.64	49	2.60	79	4.22	4.47	2.60	0.38	1.90
18	91	4.89	49	2.93	72	3.22	3.45	1.80	0.33	1.43
19	95	4.45	51	2.55	75	2.59	2.77	1.43	0.29	1.40

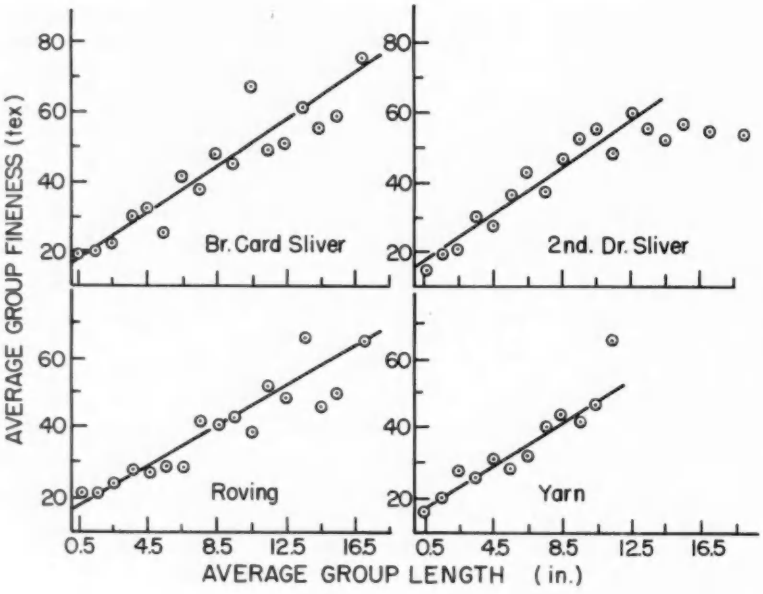

Fig. 5. Length–fineness relations of filaments at different stages of jute yarn manufacture.

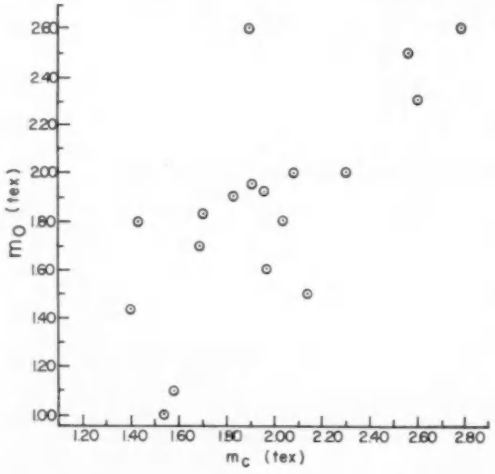

Fig. 6. Sample average of filament fineness (m_c) of combed raw jute is correlated with intrinsic fineness (m_0) of filaments in the corresponding yarn.

weight basis, are shown in Figure 7. The numerical distribution has a lower modal length and gives an average length about half the weight-average length, as the results in Table V indicate.

The group frequencies beyond the modal length suggest that the numerical distribution function is of exponential nature, while the low values of frequencies below the mode indicate the superposition of another function which diminishes as length diminishes.

This can be explained on the basis of the fact that filaments are the products of splitting of the loops in the mesh structure of the fiber and of breakage of the resulting filaments. The length of the loops has been found to be distributed approximately exponentially [3]; the distribution of filaments obtained by the breakage of weak zones in longer filaments has also been proved to be exponential by Spencer-Smith and Todd [11]. The splitting action depends on the probability that a card pin will enter into a loop; this probability will be proportional to loop length and hence to some function of filament length (l), vanishing at some point in the short length region. l^p may be taken as such a function, p being a constant for a fiber sample and depending mainly on the arrangement of pins and their motion.

The numerical distribution of filament length may therefore be expressed as

$$Y = Y_0 l^p e^{-al} \qquad (2)$$

where a, p, and Y_0 are constants, and had values 0.739 in.$^{-1}$, 0.81, and 61.9 (when Y is expressed as percentage) respectively as computed for the case plotted in Figure 7. The equation is a good fit to actual distributions; in most cases χ^2 was low enough to give $P > 0.99$.

Since the weight of filaments in a length group is simply the product of length (l), group fineness (m_l), and the number (Y) in that group, the weight distribution of filament length may be obtained from the numerical distribution according to the following equation:

$$Y_w = l \times m_0 \left(1 + \frac{\Delta}{m_0} \cdot l\right) \times Y_0 l^p e^{-al} \qquad (3)$$

which reduces to

$$Y_w = b(l^{p+1} + c \cdot l^{p+2}) e^{-al} \qquad (4)$$

where b and c are two other constants. From Equations 2 and 3, the ratio of weight average to numerical average can be shown to be equal to

$$\frac{m_0 a + \Delta(p+3)}{m_0 a + \Delta(p+2)} \times \frac{(p+2)}{(p+1)}$$

By use of appropriate values for the constants this ratio has been found to agree well with the actual ratio.

Summary

In a standard jute processing system, the weight average of filament length diminishes gradually from about 10 to 5 in. as the fiber passes from the breaker card sliver to the yarn stage. The length distribution is positively skew in each stage.

Although the varietal differences in the length parameters are largely reduced when yarns are compared, the small differences which do exist in the yarn stage are partly related to fiber quality.

In all stages the linear density of filament, along with its adherents, increases with length. The intrinsic fineness (fineness at very short length) does not alter appreciably during processing but is fairly correlated with the fineness quality of raw fiber measured on hand-combed fiber cut to 2-mm. pieces.

Acknowledgment

The authors' thanks are due to Dr. P. B. Sarkar, Director, for his interest in the work and permission to publish the results.

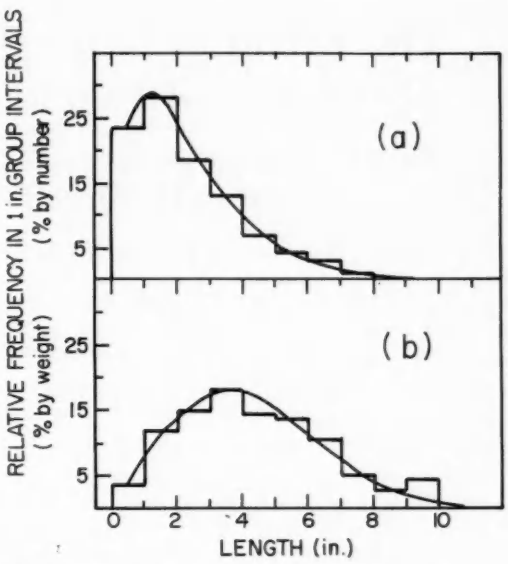

Fig. 7. Length distribution of filaments in yarn, by number (a) and by weight (b). Histograms are for 1-in. group intervals.

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The Effect of Short Fibers in a Cotton on its Processing Efficiency and Product Quality

Part II: Yarns Made by Miniature Spinning Techniques from Differentially Ginned Cotton

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Southern Regional Research Laboratory,[1] New Orleans, Louisiana

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Abstract

The conclusions reached by means of miniature spinning techniques with very small samples of cotton were similar to those obtained in Part I: changes in short fiber content do not affect the twist required for maximum strength but do lower strength somewhat more than 1% for each 1% increase in short fiber content.

These samples covered an exceptionally wide range of short fiber contents, from less than 1% to almost 20% by weight of fibers ¾ in. and shorter. The very low short fiber content cottons were produced by careful hand ginning techniques while the remainder were obtained by differential ginning techniques.

Introduction

The effects of adding to cottons with genetically low short fiber content varying proportions of short fibers were discussed in Part I of this series [7]. Similar experiments conducted with Acala 44 (Arizona) cotton samples in which differences in short fiber content were obtained by special ginning techniques are reported here. These techniques permitted the study of the effect of reducing the short fiber content very much below that reported in Part I of this series as well as at higher levels. Other workers have reported large differences in short fiber content in cotton as a result of ginning techniques. For the most part, these differences were probably the result of heat, cleaning, and other operations not resorted to in obtaining samples for this experiment [6, 8, 9]. Three samples in this experiment necessarily included very small quantities of cotton. For this reason, miniature spinning techniques described by Landstreet et al. [4] were used for processing all samples.

Experimental Procedure

Hand ginning was used to obtain samples of cotton with very low short fiber contents. The cotton fibers on the seed were butterflied and the loose fibers were combed out. These combings were retained and are termed "Combed from Seed" in this series of experiments. The butterflies, with the loose fibers removed by combing, were ubjected to three gentle plucks of only the longer fibers from each side of the seeds. Only about ½ lb. of cotton fibers was produced by combing or plucking from butterflied seed because of the tediousness of the process. These plucks are designated as "Plucked from Seed." Other samples of cotton from the same lot of seed cotton included normal machine ginning and three levels of differential ginning; the method of differential ginning is discussed in detail in the paper by Griffin et al. [3]. Briefly, the method consists of holding the seed cotton in the seed box of an operating saw gin for various periods of time before dumping. The periods were 24, 27, and 30 sec. for the samples used in this ex-

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] One of the field stations of the Crops Research Division, Agricultural Research Service, U. S. Department of Agriculture.

periment. The cotton fibers removed in the first pass of the seed cotton held 27 sec. are termed 1-27, and so forth. Cotton fibers from this same lot of seed cotton removed by a second pass through the gin are termed 2-27, and so forth. The fiber tests were performed in accordance with ASTM procedures except that length groups from the sorter were not placed on velvet boards [1].

"Completely hand ginned" samples were also prepared by removing all the lint possible from each seed by hand. Such samples had short fiber contents ($\frac{3}{8}$ in. and shorter) of approximately 4% by weight. However, spinning replicate lots of this hand ginned cotton resulted in such large strength variations in the yarns that these data are not presented. The cause of this extreme variability is not known, although it is suggested that because of the seed-by-seed ginning the lint from each seed tended to stay together and the variability observed in yarn strengths might thus be the result of the large variation in the properties of fibers removed from different seeds which is normally masked out by the simultaneous ginning of many seeds. Ascertaining precisely the cause is beyond the scope of this study.

All lots of cotton were processed into 27 tex (22/1) yarn using a range of twist rates. Yarn strength was measured with the Uster Single Strand tester [3] and by the miniature skein test as described by Landstreet et al. [4]. Only single strand tests were made on the hand ginned cotton samples.

The twist tenacity curves were typical for all samples; it was possible to express the experimental data for each sample by a symmetrical second degree polynomial curve of the general form

$$Y = A + BX + CX^2$$

where Y = yarn tenacity and X = yarn twist multiplier. One curve from this experiment is shown in Figure 1. The constants A, B, and C were determined for each sample and the resulting equation differentiated to determine the twist multipliers which gave the maximum tenacity. The maximum tenacity was then determined from the regression equation. A symmetrical curve could be fitted to the twist–strength data in this experiment because of the limited range of twists used. For a wider range of twists the twist–strength curve would be highly asymmetrical and a curve of a different general form would be used.

[3] Use of a company and/or produce named by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

Results and Discussion

The methods of differentially ginning cotton used produced samples that varied in both upper quartile length and length distribution. The upper quartile mean and percent of fibers less than $\frac{3}{8}$ in. long are listed in Table I. The decrease in length with increased ginning time is not fully accounted for by the increase in percent fibers less than $\frac{3}{8}$ in. long. Part I of this series showed that when various percentages of short fibers were added to a base sample there was no appreciable decrease in upper quartile lengths and the change in the mean length was moderate [6].

Admittedly, methods of differential ginning might produce different fiber length distributions than are obtained by the addition of short fibers. A limited investigation was made to determine whether the concept of random breakage as proposed by Byatt and Elting would explain the length distributions actually obtained [2]. The results were somewhat disappointing. However, this is not too surprising, since the evidence indicates that differential ginning is not a random breakage phenomenon. Griffin et al. show that the process appears to be one of selective ginning [3]. Further research to determine a satisfactory model for the length distributions obtained by differential ginning is needed.

The reduction in length for the samples in this experiment, while not desirable, was unavoidable with the ginning techniques used. For the samples listed in Table I, the ranges in upper quartile and

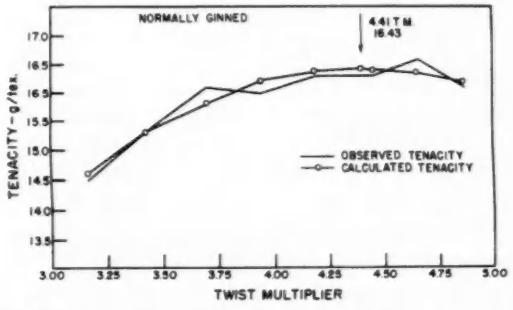

Fig. 1. Single strand tenacity vs. twist multiplier for a typical cotton showing degree of fit between actual values and curvilinear correlation curve.

TABLE I. Effect of Short Fiber Content and Upper Quartile Length on Yarn Tenacity and the Twist Multiplier Necessary for Maximum Single Strand Tenacity of 27 tex (22/1) Yarn Spun from Acala 44 Cotton

Sample	Short fibers 3/8 in. and less, % weight	Upper quartile, in.	Mean, in.	Twist multiplier for maximum tenacity			Tenacity (maximum), g./tex			Multiple correlation coefficient	
				Rep. 1	Rep. 2	Mean	Rep. 1	Rep. 2	Mean	Rep. 1	Rep. 2
Plucked from seed	0.87	1.31	1.18	4.44	4.19	4.32	18.7	18.7	18.7	.95	.63
Combed from seed	2.16	1.27	1.11	4.15	4.40	4.28	18.4	18.1	18.2	.72	.92
Differentially ginned First pass											
1–24	4.62	1.20	1.00	4.39	4.40	4.40	17.7	17.6	17.6	.98	.85
1–27	3.99	1.23	1.05	4.41	4.89	4.65	17.7	17.7	17.7	.84	.93
1–30	4.32	1.23	1.04	4.44			17.7			.97	
Normally ginned	7.61	1.22	1.00	4.41			16.4			.97	
Differentially ginned Second pass											
2–24	18.93	1.11	.81	4.77			14.0			.99	
2–27	19.95	1.11	.80	4.61			14.7			.99	
2–30	12.38	1.12	.87	4.70			13.2			.95	

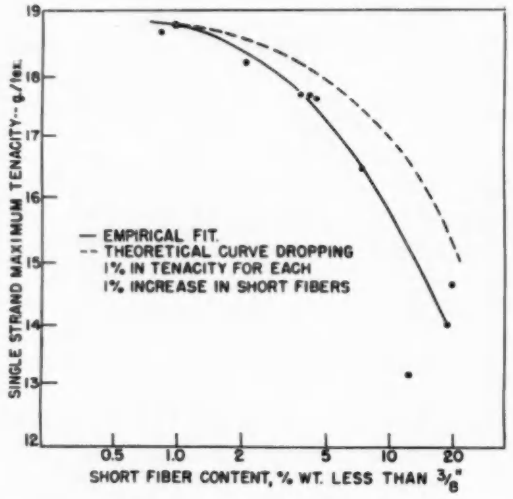

Fig. 2. Single strand tenacity vs. short fiber content for Acala 44 cotton.

mean length were 0.20 in. and 0.38 in. and the range in percent fibers less than 3/4 in. long was 19.

The nine samples in Table I can be combined into three classes on the basis of upper quartile length. Associated with these three length groupings are similar groupings of twist multipliers required to produce maximum single strand strength. It was shown in Part I of this series that the addition of fibers less than 3/4 in. did not affect the twist multiplier. The data presented in Part I and in Table I of this paper show that the twist multiplier required for maximum strength is primarily a function of the upper quartile length of the cottons evaluated.

The short fiber content versus single strand maximum tenacity is shown in Figure 2. The solid line was drawn to the observed data. The dashed line is a calculated curve showing the expected decrease in yarn tenacity with increase in percent short fibers assuming the short fibers contribute nothing to yarn tenacity. (Coincidence was arbitrarily set at 1% short fiber content.) It can be seen that the actual decrease in yarn tenacity is greater than expected. This difference cannot be justified on the basis of reduced fiber length or fiber tenacity. The fiber tenacity for all samples was approximately 19.5 g./tex. Landstreet has indicated that the range in upper quartile length of 0.20 in. is too small to change appreciably the maximum yarn tenacity [5].

The pattern exhibited by the single strand data is substantially repeated for the skein data, although characteristically the twist for maximum strength is somewhat lower. The conclusions that could be drawn from skein data essentially replicate those derived from single strand data. In each lot single strand elongation increased with twist, as would be expected. There was nothing of special interest to report on this property.

The short fibers thus appear not only to add useless bulk to the yarn but also to prevent the working fibers from performing at their maximum potential.

Future work to be reported in this series will in-

clude data on the effect that short fibers have on spinning efficiency and fabric properties.

Conclusion and Summary

The results obtained here corroborated the results reported in Part I where varying percentages of short fibers were added to normally ginned cottons. Increasing short fiber contents through the use of special ginning techniques was found to be detrimental to yarn tenacity; the effect was discernible even for small increases at low levels of short fiber content. Decreases in tenacity were greater in relation to increases in short fiber content than could have been expected if the assumption had been made that these fibers were merely inert weight. Short fibers, at least in the levels investigated and within the precision available from such small samples, do not seem to affect the twist required for maximum strength.

Acknowledgment

The authors express their appreciation to those staff members of the Southern Regional Research Laboratory, New Orleans, Louisiana and the U. S. Department of Agriculture Spinning Laboratory, Knoxville, Tennessee who performed the necessary processing and testing of the samples in this study.

Appreciation is also expressed to the Agricultural Engineering Research Division, Beltsville, Maryland and the U. S. Department of Agriculture Ginning Laboratory, Mesilla Park, New Mexico for providing the special ginning techniques.

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Letters to the Editor

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Partially Cross-Linked Viscose Rayon Nitrate

Yatsushiro Laboratory
Kōkōku Rayon & Pulp Co., Ltd.
Yatsushiro, Kumamoto, Japan
May 16, 1960

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Rayon has defects in elastic recovery and water resistance (high degree of swelling, high moisture regain, and low wet modulus).

Various methods, such as resin finishing and esterification, were attempted to improve these properties. It is well known that formalin treatment causes cross-linking, reduces swelling, and increases wet strength but has the disadvantages of making the fiber brittle [2]. Attempts have been made to increase the length of cross-linking by using a higher dialdehyde, but improvement in mechanical properties was small [1].

Simultaneous use of partial acetalization and fibrous nitration [4] has also been studied. Acetalization will reduce the degree of swelling by cross-linking between molecular chains and esterification will reduce polarity to prevent the fiber from becoming brittle and to reduce moisture absorption. Also, acetalization probably suppresses macro-Brownian motion of the molecules while esterification assists micro-Brownian motion of the segments to make the structure resemble that of vulcanized rubber and so increase elasticity.

In the current study, the sample used was crimped rayon staple of 5 den. × 3 in. before oiling.

For acetalization, the sample was steeped in an aqueous solution of glutaraldehyde containing magnesium chloride catalyst, centrifuged to 100% pick-up, pre-dried, cured for 30 min. at 140° C., washed with water, then washed with soap solution.

In nitration, the nitrogen content was controlled by reaction time or the amount added of a mixture of

TABLE I. Characteristics of Fiber Treated with Glutaraldehyde after Partial Nitration

(Mixed acid: HNO_3 10%, Ac_2O 10%, CCl_4 80%)

Nitrating time, min.	None	80			120		
Aldehyde conc., %	None	None	3	4	None	4	5
Nitrogen content, %	0	2.77	2.77	2.77	6.43	6.43	6.43
Degree of swelling, %	77.1	54.8	45.2	41.6	37.4	23.0	19.0
Moisture regain, %	13.5	10.9	—	—	—	—	—
Denier	5.73	—	6.34	6.33	—	7.55	7.66
Dry strength, g./den.	2.17	—	1.97	1.85	—	1.54	1.40
Dry elongation, %	14.3	—	12.2	11.0	—	9.1	7.6
Knot strength, g.	4.62	—	4.32	4.27	—	4.17	2.78
Delayed elastic recovery at 5% stretch, %	54.3	—	70.4	64.5	—	84.9	86.1

acetic anhydride and nitric acid (1 : 1) with carbon tetrachloride. The sample, which was conditioned to ca. 25% moisture, was nitrated and then washed with methanol and water.

The degree of swelling of the product was measured as the percentage of increase in weight after centrifuging. Moisture regain was determined after conditioning for 72 hr. at 20° C. and 65% RH and expressed on the dry basis. Tenacity and elongation were measured by the JIS [1] method with the McKenzie Tester, instantaneous elastic recovery by an Instron Tester (deforming speed, 50%/min.), delayed elastic recovery with a specially designed tester (relaxed immediately and measured after 3 hr. under initial tension of 0.3 g./den.). Nitrogen content was determined by colorimetry [3].

Results of reversing the sequence of treatment are shown in Tables I and II.

The degree of swelling is reduced even when acetalization and nitration are made individually, but it is lowest when the sample is acetalized after nitration.

When this sequence was reversed, the degree of swelling, reduced by acetalization, returns somewhat to the initial value at low nitrogen content, but decreases again at high nitrogen content.

Acetalization has little effect on moisture regain, which, however, is reduced in accordance with nitrogen content.

Dry and wet strength are not reduced very much, but tenacity per denier is reduced as fineness (denier) increases with increase in nitrogen content. Knot strength is reduced considerably with acetalization, but recovers when the fiber is nitrated afterwards. The product, which is not excessively acetalized after nitration, has knot strength similar to that of the original sample. Thus, brittleness by simple cross-linking can be prevented.

Instantaneous and delayed elastic recovery are improved considerably by the combined treatment; there is little difference due to treatment sequence and degree of acetalization, but results are better with more intensive nitration.

As there is a possibility of breaking the cross-linking when the fiber is nitrated after the acetalization, it appears better to nitrate first. However, since the difference is not large, the sequence should be decided after taking into consideration the convenience in an industrial-scale production.

Thus, if cross-linking and nitration conditions are combined appropriately, it is possible to improve the poor wrinkle recovery and water resistance which are the defects of rayon.

The authors plan to carry on research on other esterifications, such as acetylation and cross-linking methods.

[1] Japanese Industrial Standards.

TABLE II. Characteristics of Fiber Partially Nitrated after Treatment with Glutaraldehyde

Dilution ratio (CCl_4), %			94	88
Nitrating time, min.	None	None	30	60
Aldehyde conc., %	None	5	4	5
Nitrogen content, %	0	—	1.91	6.44
Degree of swelling, %	73.7	44.8	61.6	36.0
Moisture regain, %	13.3	13.6	11.8	7.3
Denier	5.56	5.48	5.69	6.69
Dry strength, g/den.	2.35	2.37	2.28	1.94
Dry elongation, %	15.1	13.9	16.4	12.8
Knot strength, g.	5.27	2.17	7.53	5.34
Delayed elastic reovery at 5% stretch, %	62.8	75.3	65.7	74.4
Elastic recovery at 5% stretch, %	30.3	—	—	43.3

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Toshikazu Fujimura
Shin'ichi Okamoto

On Tensile Properties of Alkali-Treated Jute Fibers

Institute for Fibres and
Forest Products Research
Jerusalem, Israel
May 31, 1960

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The formation of crimp on jute fibers under alkali treatment was investigated and presented in a previous paper [3]. The crimp was defined by two parameters—the crimp diameter D and the wave number n—of the crimped fibers and measured according to a method described elsewhere [1]. The uncrimping energy of extension of crimped jute was also evaluated in the above work [3], and a comparison has been made between the values obtained and some published results from wool samples. It was found that the maximum values of the crimp parameters were obtained when the treatment was carried out at 2° C. for 1 hr. and at a concentration of 9% NaOH. The extension at break of the crimped jute fibers was measured and described as the ratio of the total extension to the "initial" length at a load of 10 mg.

Roy [6] studied the mechanical properties of jute fibers chemically treated at room temperature (90° F.). The values of the tenacity and the extension at break found by Roy are for this temperature. Roy observed a "wool-like appearance" in some samples of the treated jute fibers. However, it was shown in our previous communication [3] that the crimp parameters at this temperature are considerably lowered and that no crimp was observed on jute samples treated at 40° C. and higher temperatures when the alkali concentration was 9%.

Roy observed an abrupt rise in extension at break when increasing the concentration of alkali above 9%. A considerable increase in extension was also found by MacMillan et al. [4] (Table IX) for jute fibers treated with 15% alkali for 10 min. at 22° C.

No details of other mechanical properties of the treated jute fibers were presented in our previous communication. Some results of measurements of tenacity, extension at break, and Young's Modulus of the jute fibers are reported in the present communication.

The tensile properties of untreated fibers and of fibers treated with 5, 9, and 24% NaOH for 1 hr. at 2° C. were measured. These samples are designated 0k, 5k, 9k, and 24k and correspond to the similarly labeled samples in the previous work [3].

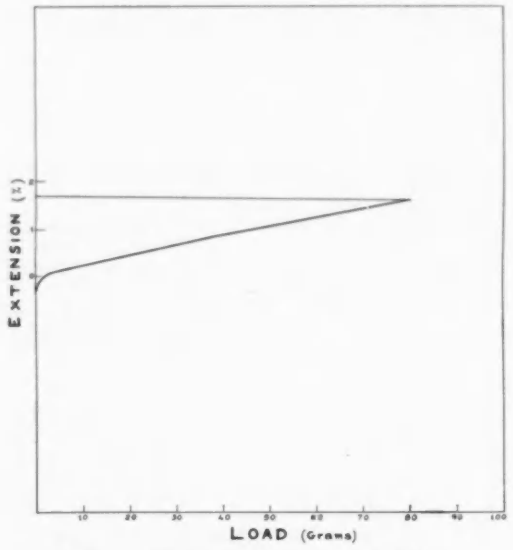

Fig. 1. Load–extension curve; Sample 0k.

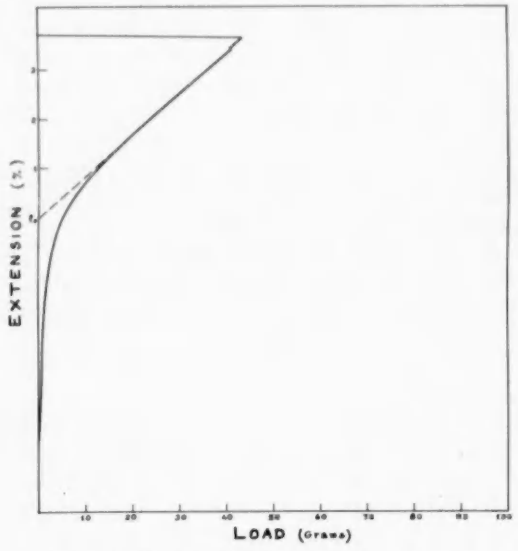

Fig. 2. Load–extension curve; Sample 9k.

TABLE I. Tensile Properties of Jute Fibers

Sample		Tenacity g./den.	Tenacity CV	Extension at break %	Extension at break CV	Y.M. g./den.	Y.M. CV	Uncrimping stress Mg./cm.²	Uncrimping stress CV
0k	Not crimped	3.56	36.2	1.20	26.7	296.0	23.0		—
5k	Not crimped	3.27	30.9	1.32	31.2	268.1	31.6		—
9k	Crimped	2.52	31.6	3.61	38.0	77.6	31.2	0.252	24.2
24k	Crimped	1.48	26.5	3.40	29.5	46.1	33.8	0.231	29.5

All tests were carried out in an air-conditioned room at 70% RH and 20° C. First, the mass per unit length of the fibers was determined vibroscopically. In order to minimize the effect of the fiber's crimp when the fiber's length was of the order of 4 cm., a weight of about 1.5 g. was attached to the fibers. From these measurements the cross-sectional areas and the denier values were calculated. The density of jute was taken as 1.47.

The same fibers were then extended on the Instron Tensile Tester at a rate of extension of 0.2 cm./min. with test lengths of 4 cm. Stress–strain data were calculated from the Instron charts as shown in Figures 1 and 2. Twenty-five single fiber determinations were averaged to obtain the breaking tenacity, extension at break, and Young's Modulus for each sample.

The points of zero extensions (Figures 1 and 2) were chosen in a similar way to the method used in the case of wool fibers; i.e., through the intercept of the extrapolated Hookean slope and the extension axis. In the case of Samples 9k and 24k, which are crimped, the uncrimping region is clearly observed, as shown in Figure 2 for Sample 9k; also the slope of this curve is considerably distinct from the slope of the curve of Figure 1, which corresponds to a not-crimped sample.

In Table I the effect of the percent concentration of alkali on the tensile properties is given.

Table II contains the significance tests carried out between samples.

It is seen from Table I that the tenacity values decrease with concentration. A similar decrease was found by Roy [6] when the fibers were treated at 90° F.

The extension at break reached a maximum value of 3.61% at 9% NaOH.[1] With further increase in concentration there is a trend for a decrease in the extension. Roy [6] found an abrupt rise in the extension at break at a higher concentration (at 90° F.). It follows that Young's Modulus decreases sharply from 0 to 9% NaOH; further increase in the NaOH concentration causes only a small further decrease, whereas Roy's results show a sharp decrease up to 12% NaOH.

[1] In the previous work [3] the extension at break was obtained in a different way and described as the ratio of the final extension to an initial length at a load of 10 mg. (see Table III in [3]).

TABLE II. Significance Tests at 95% Level of Confidence

Between samples	Tenacity	Extension at break	Y.M.	Uncrimping stress
0 – 5k	—	—	—	—
5k– 9k	+	+	+	+
9k–24k	+	–	+	–

The uncrimping energies of the samples are given in Table I. These values were obtained from the Instron charts and resemble the results obtained in the previous work (Table III) by an integration method.

Rebenfeld and Virgin have found in the case of cotton a significant correlation between the x-ray angle and single fiber properties such as Young's Modulus and breaking elongation. Sen and Chowdhury [7] observed that, in the case of jute, "the orientation factor and the angle at 40% intensity have no correlation with the intrinsic strength, but there is a slight correlation if the two varieties of jute—White and Tossa—are taken separately." Gupta [2] has also found that, for native jute treated with up to 30% NaOH, the Herman's orientation factor decreases. Therefore, it seems that a correlation exists between single jute fiber properties and the x-ray angle. It is suggested that changes in single fiber properties of alkali-treated fibers are due to changes in the crystallite orientation resulting from this treatment; it is also possible that the crimp formation is related to the variation in this crystallite orientation of the single fibers as caused by alkali treatments.

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J. BANBAJI

Differential Thermal Analysis of Protein Fibers

Textile Research Institute
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May 31, 1960

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Some new results have been obtained on the thermal behavior of protein fibers by means of differential thermal analysis (DTA). DTA involves the measurement of the thermally detectable transitions or reactions that occur as a substance is heated at a constant rate through the temperature range of interest and the general technique has been well described in the literature [5, 7]. The application of this technique to textile fibers was the subject of a recent communication to this journal [6].

Fiber samples of about 150 mg. were heated at a rate of 10° C./min. from room temperature to 550° C. Calcined aluminum oxide was employed as the thermally stable reference material. The apparatus and specific techniques used are fully discussed in a paper to be submitted for publication in this journal. The properties of the keratin fibers examined are described in detail elsewhere [2]. In Figure 1 the DTA curves obtained under a nitrogen atmosphere are shown for a series of protein fibers. The major reactions are indicated to be endothermic for all the fibers and, of course, nonoxidative in nature. The keratin fibers as a group yield similar curves and are distinguished from the curve for silk in the temperature range in which the second major reaction appears to occur (326° C. for silk) and in the shape and depth of the peaks. It is suggested that this difference may be due to the melting or disordering of α- and β-keratin. Silk is known to consist of polypeptide chains in a predominantly extended configuration with intermolecular hydrogen bonding and having a general resemblance to β-keratin. Keratin fibers in their natural state consist essentially of α-keratin, although some work [1, 3] has indicated that small amounts of β-keratin may be present. All the curves show an initial reaction which is endothermic and show peak temperatures ranging from 108° C. for silk to 116° C. for human hair. In each case, this reaction represents the loss of sorbed water. As the curves return to the base line, a small shoulder appears about 160° C. which is evidence for a second endothermic reaction of a minor nature. Watt et al. [8] have recently shown that a small amount of absorbed water in wool fiber is strongly held at hydrophillic sites in the fiber and is removed only at relatively high temperatures (up to 150° C. *in vacuo*). Thus this second and smaller endothermic reaction may represent the removal of this tightly held water.

In the keratin fibers, the next major reaction is also endothermic and begins around 210° C. A single peak at 251° C. is observed for human hair, whereas in the case of IWS Wool C (an Australian Merino wool) and kid mohair the shape of the endotherms suggests that at least two sequential reactions have occurred. No major reaction appears to occur in the temperature range of 210°–275° C. in silk. Silk shows an important endothermic reaction starting gradually around 275° C. and accelerating rapidly at 285° C. to reach the peak at 326° C. It is of interest to note that, in the keratin fiber curves, small endothermic deflections appear in this temperature region with peaks at 320° C., 324° C., and *ca.* 316° C. for mohair, wool, and hair respectively. It is thought that these small endothermic reactions may arise from the melting of the β-keratin com-

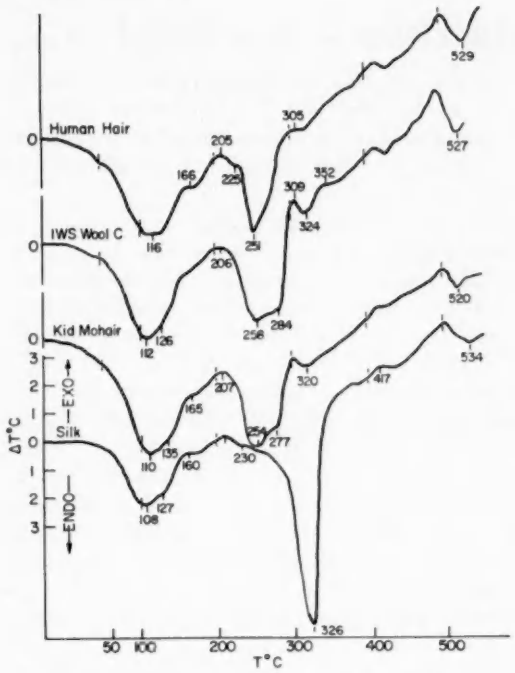

Fig. 1. Thermograms of protein fibers in nitrogen.

ponent. The suggestion that the endothermic reactions occurring during the heating of these protein fibers subsequent to the loss of sorbed water represent melting reactions is supported by the available thermogravimetric data. These data show weight losses of only 9.5% for silk up to 315° C. and *ca.* 12% for a keratin fiber (Vicuna) up to 270° C. Such relatively small losses do not suggest chain degradation or depolymerization; however, until more data by both DTA and TGA (thermogravimetric analysis) are available, the possibility that these endotherms represent depolymerization of the polypeptide chains cannot be excluded.

Another explanation for the differences observed in the shapes of the second major endotherms appearing in keratin fiber curves may be associated with their ortho–para structure. Human hair, showing a single peak, is essentially all para; IWS Wool C, with two almost equal peaks, is ortho–para; and kid mohair, with two unequal peaks, is primarily ortho with para as the small component. A third possibility arises from the recent work of Feughelman and Haly, wherein two zones of different thermal stability along the microfibrils in wool keratin were proposed [4]. The appearance of the wool endotherm with the first peak at 258° C. and an indication of a second reaction at 284° C. is consistent with their model, as are the corresponding data for kid mohair. The absence or near absence, however, of such a second reaction at 284° C. for human hair would appear to be inconsistent with the proposed "two-zone model" of Feughelman and Haly [4]. In any event, it is not possible at this time to present more than the foregoing speculations regarding the apparently double-peaked endotherms found for wool and mohair.

We are grateful for comments by M. Feughelman of the Australian CSIRO. We are also indebted to L. R. Beck, Jr. and E. B. Jefferies for assistance in obtaining the experimental measurements.

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Preparation of Partially Benzhydrylated Cotton Cellulose[1]

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May 2, 1960

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

In a program of study designed to demonstrate fundamental relationships of cellulose etherification and mechanical properties of textiles, the benzylation of mercerized cotton was investigated [5]. The fibrous products prepared during that study with a degree of substitution less than one [2, 5] retained many of the desirable mechanical properties of cotton and in addition showed increases in elastic recovery, decreases in permanent set, a high degree of thermoplasticity, and the formation of a new crystal lattice for benzylcellulose.

In an extension of the study it seemed desirable also to prepare benzhydryl and trityl cellulose of similar degrees of substitution and to determine how the systematic substitution of phenyl groups for hydrogens might affect the mechanical properties. The present paper describes studies undertaken to develop a suitable method for the benzhydryl reaction. The primary goal was to devise a method which would be suitable for the preparation of yarns having degrees of substitution in the range from zero to one. The properties of such benzhydrylated yarns could then be compared with those of benzylated yarns having approximately the same degrees of substitution.

The water–alcohol–sodium hydroxide–organic halide method, used in the preparation of benzylated cotton by Klein et al. [5], was tried and found to be unsuitable for the preparation of benzhydrylated cotton. It was found that the organic halide reacted preferentially with the aqueous solution on the cotton and by hydrolysis liberated enough acid to degrade the cellulose. Yarns rubbed with a solution of water, alcohol, and sodium hydroxide and then heated at 95° with benzhydryl chloride or bromide were not only degraded to a powder, but also failed to give the characteristic yellow color of the benzhydryl ion [1] when dissolved in concentrated sulfuric acid.

The pyridine–organic halide method used by Hearon et al. [3] for the production of tritylated cellulose was also tried and found to be unsuitable. Pyridine-exchanged yarns when treated with benzhydryl bromide or chloride in pyridine at 100° for 5 hr. retained their fibrous structure, but only a trace of benzhydryl groups was introduced. The maximum weight gain was 2% and only a slight color was obtained in the sulfuric acid test. Crystals which separated from one of the chloride reaction mixtures were water soluble and had a melting point of 199°. This was the same melting point as that obtained for a freshly prepared and analyzed sample of benzhydryl pyridinium chloride. Apparently, the organic halides react mainly with the pyridine to form the stable quaternary salts.

It was hoped that stable salt formation could be overcome by using a substituted pyridine. Reynolds and Kenyon [7] found that the tendency to quaternize with simple sulfonic esters decreases in the order 2-methylpyridine > 2,4-dimethylpyridine > 2,6-dimethylpyridine (2,6-lutidine). The methyl groups flanking the nitrogen in the 2,6-lutidine cause the base to be sterically hindered and hence resistant to quaternization. With this fact in mind, test benzhydrylations were carried out using 2,6-lutidine in place of pyridine. Both benzhydryl chloride in 2,6-lutidine and benzhydryl bromide in 2,6-lutidine were used for the etherification of cellulose. The latter combination produced a more rapid reaction and readily led to the production of benzhydrylated yarns with degrees of substitution in the range from zero to one and above. Apparently stable quaternary salt formation does not occur with the 2,6-lutidine.

Experimental

Materials

Eastman White Label[3] benzhydryl chloride was used as received. Benzhydryl bromide was syn-

[1] Paper presented before the Division of Cellulose Chemistry, American Chemical Society, Cleveland, Ohio, April 5–14, 1960.

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[3] Use of a company and/or product name by the Department does not imply approval or recommendation to the exclusion of others which may also be suitable.

TABLE I. Effect of Reaction Time on Benzhydrylation of Cotton Yarn with Benzhydryl Chloride in Lutidine at 100° and 120°. Mole Ratio of Cellulose:Benzhydryl Chloride:Lutidine, 1:10:23

Reaction time, hr.	100° C.		120° C.	
	Weight gain, %	DS	Weight gain, %	DS
1	3.9	0.04	15.0	0.15
2	6.5	0.06	19.9	0.19
3	9.2	0.09	28.2	0.28
4	11.5	0.11	33.9	0.33
5	13.0	0.13	38.6	0.38

TABLE II. Effect of Reaction Time on Benzhydrylation of Cotton Yarn with Benzhydryl Bromide in Lutidine at 100° and 120°. Ratio of Cellulose:Benzhydryl Bromide:Lutidine, 1:9:23

Reaction time, hr.	100° C.		120° C.	
	Weight gain, %	DS	Weight gain, %	DS
1	23.5	0.23	69.9	0.68
2	33.4	0.33	88.3	0.86
3	44.9	0.44	102.1	1.00
4	53.0	0.52	118.7	1.16
5	58.6	0.57	128.5	1.25

thesized by the bromination of diphenylmethane according to the method of Norris et al. [6]. Cotton was in the form of commercially mercerized linker yarn (7/2). Reagent grade pyridine was used as received. Practical grade lutidine was redistilled before using.

Benzhydrylation in 2,6-Lutidine

With the important exception that 2,6-lutidine had to be substituted for pyridine, the reaction conditions were patterned after those which Hearon et al. [3] and Honeyman [4] had used successfully in their tritylation studies.

One-gram skeins of air-dried cotton yarns (7/2) were activated with 17.5% sodium hydroxide, washed with water, 5% acetic acid and water, then pyridine-exchanged. The exchanged yarns were washed three times with 2,6-lutidine, centrifuged, and then added to a reaction mixture of benzhydryl chloride or bromide in 2,6-lutidine. When benzhydryl chloride was used the mole ratio of cellulose: organic halide: lutidine was 1:10:23. When the bromide was used this ratio was 1:9:23. After the reaction mixture was heated at 100° or 120° for the desired time the insoluble products were washed with pyridine, methyl alcohol, and water. The yarns were then oven-dried at 115°. The effect of reaction time on benzhydrylation with benzhydryl chloride at 100° and 120° is given in Table I. The same effect with benzhydryl bromide at 100° and 120° is presented in Table II.

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